

# FINAL REPORT

Evaluation of Perchlorate Sources in the  
Rialto-Colton and Chino California Subbasins using  
Chlorine and Oxygen Isotope Ratio Analysis

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## Table of Contents

<b>List of Figures.....</b>	<b>v</b>
<b>List of Tables .....</b>	<b>vii</b>
<b>List of Acronyms and Abbreviations .....</b>	<b>viii</b>
<b>Abstract.....</b>	<b>1</b>
<b>1.0 Introduction.....</b>	<b>3</b>
1.1 Perchlorate Sources.....	3
1.1.1 Synthetic Perchlorate .....	4
1.1.2 Atacama Nitrate Deposits and Fertilizer .....	4
1.1.3 Indigenous Natural Perchlorate in the US.....	5
1.2 Location and Characteristics of the Study Area .....	7
1.3 Isotopic Analyses of $\text{ClO}_4^-$ .....	9
1.3.1 Stable Isotope Ratios of Cl and O in Synthetic $\text{ClO}_4^-$ .....	11
1.3.2 Stable Isotope Ratios of Cl and O in Atacama $\text{ClO}_4^-$ .....	12
1.3.3 Stable Isotope Ratios of Cl and O in Indigenous Natural $\text{ClO}_4^-$ .....	14
1.4 Abundance of $^{36}\text{Cl}$ in Synthetic and Natural Perchlorate .....	17
<b>2.0 Materials and Methods.....</b>	<b>20</b>
2.1 Selection of Wells for Groundwater Sample Collection.....	20
2.2 Groundwater Sampling Procedure .....	21
2.3 Sample Purification and Isotopic Analysis .....	24
2.3.1 Sample purification .....	24
2.3.2 Analysis of Oxygen Isotope Ratios in Perchlorate by IRMS.....	25
2.3.3 Analysis of Chlorine Isotope Ratios in Perchlorate by IRMS .....	27
2.3.4 Standards for Oxygen and Chlorine Stable Isotopic Analysis .....	28
2.3.5 Analysis of $^{36}\text{Cl}$ in $\text{ClO}_4^-$ .....	30
<b>3.0 Results and Discussion .....</b>	<b>31</b>
3.1 $\text{ClO}_4^-$ Concentrations in Groundwater Wells.....	31
3.2 Isotope Results for $\text{ClO}_4^-$ .....	31
3.3. Depth-Dependent Isotope Samples.....	52
3.4 Data Quality and Reproducibility .....	53
3.4.1 Results from Replicate Columns .....	54
3.4.2 $\delta^{18}\text{O}$ from $\text{O}_2$ -DI-IRMS( $-\text{N}_2$ ) and CO-CFIRMS .....	54
3.4.3 Perchlorate Extraction and Purification – Method Tests for QA/QC .....	55
3.4.4 Secondary Ion Mass Spectrometry (SIMS) .....	56

3.5 Summary and Conclusions .....	61
<b>4.0 Acknowledgments.....</b>	<b>63</b>
<b>5.0 References Cited.....</b>	<b>63</b>
<b>Appendix A: Perchlorate Extraction and Purification - Method Tests for QA/QC</b>	
<b>Appendix B: Comparison of Cl and O Stable Isotope Values in ClO<sub>4</sub><sup>-</sup> by SIMS and IRMS</b>	

## List of Figures

- Figure 1.1. Overhead view of the Study Area with the two previously identified source areas and the associated perchlorate plumes delineated.
- Figure 1.2. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in natural indigenous  $\text{ClO}_4^-$  of the US Southern High Plains (black and white squares) and Death Valley caliche (black triangles), natural Atacama  $\text{ClO}_4^-$ , (blue diamonds for caliche and groundwater and green diamonds for nitrate fertilizer samples) and synthetic  $\text{ClO}_4^-$  (red circles).
- Figure 1.3. Values of  $^{36}\text{Cl}/\text{Cl}$  (mole fraction) versus  $\delta^{37}\text{Cl}$  in representative samples of synthetic  $\text{ClO}_4^-$  reagents and products, natural  $\text{ClO}_4^-$  extracted from soil and groundwater from the Atacama Desert, Chile, and natural  $\text{ClO}_4^-$  extracted from groundwater and soil from the southwestern U.S. (modified from Sturchio et al., 2009).
- Figure 2.1. Wells selected for bulk discharge  $\text{ClO}_4^-$  isotope sampling (light blue symbols) and depth-dependent  $\text{ClO}_4^-$  isotope sampling (dark blue symbols).
- Figure 3.1. Concentration of  $\text{ClO}_4^-$  in groundwater wells during stable isotope sampling.
- Figure 3.2. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples (red closed diamonds indicate wells located within the mapped  $\text{ClO}_4^-$  plume areas and light blue closed diamonds indicate wells located outside the mapped plume areas; Figure 1.1; Table 3.1; Izbicki et al., 2014) with data for synthetic  $\text{ClO}_4^-$  (open black circles), natural Atacama  $\text{ClO}_4^-$  (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples), and indigenous natural  $\text{ClO}_4^-$  of the southwestern U.S. including Southern High Plains (SHP) and Middle Rio Grande Basin (MRGB) groundwater (black open squares) and Death Valley caliche (black triangles).
- Figure 3.3. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples within the mapped plume areas (red closed diamonds with well designations) and outside the mapped plume areas (light blue closed diamonds) with source data (symbols as described in the caption to Figure 3.2).
- Figure 3.4. Comparison of  $\delta^{37}\text{Cl}$  versus  $1/\text{ClO}_4^-$  concentration (top left panel),  $\Delta^{17}\text{O}$  versus  $1/\text{ClO}_4^-$  concentration (top right panel),  $^{36}\text{Cl}/\text{Cl}$  ( $\times 10^{-15}$ ) on log scale versus  $1/\text{ClO}_4^-$  concentration (middle left panel),  $\delta^{18}\text{O}$  versus  $1/\text{ClO}_4^-$  concentration (middle right panel) and  $^{36}\text{Cl}/\text{Cl}$  ( $\times 10^{-15}$ ) on linear scale versus  $1/\text{ClO}_4^-$  concentration (bottom middle panel), with symbols as described in the caption to Figure 3.2.
- Figure 3.5. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel);  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (middle panel) and  $\delta^{37}\text{Cl}$  versus  $^{36}\text{Cl}/\text{Cl}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples (symbols as in Figure 3.2).

Figure 3.6. Comparison of  $\delta^{18}\text{O}$  value (‰) versus  $^{36}\text{Cl}/\text{Cl}$  ratio for wells located within the mapped  $\text{ClO}_4^-$  plume areas for which both values are available.

Figure 3.7. Comparison of  $\delta^{18}\text{O}$  value (‰) versus  $\text{ClO}_4^-$  concentration (top panel) and  $^{36}\text{Cl}/\text{Cl}$  ratio vs  $\text{ClO}_4^-$  concentration (bottom panel) for all wells located within the mapped  $\text{ClO}_4^-$  plume areas for which both values are available.

Figure 3.8. Map of land use characteristics in 1949 in the Chino Basin Management Zone.

Figure 3.9. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater depth-dependent samples (symbols as in Figure 3.2) with published data for indigenous natural  $\text{ClO}_4^-$  of the SHP and MRGB (black open squares), natural Atacama  $\text{ClO}_4^-$  (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples), and synthetic  $\text{ClO}_4^-$  (open black circles).

Figure 3.10. Comparison of O isotope results from different methods.

Figure 3.11. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from individual Study Area groundwater samples analyzed for O isotopes by  $\text{O}_2$ -DI-IRMS(+ $\text{N}_2$ ) (closed red diamonds),  $\text{O}_2$ -DI-IRMS(- $\text{N}_2$ ) (closed green diamonds), or CO-CFIRMS (closed orange diamonds) with data for natural indigenous  $\text{ClO}_4^-$  of the US (open black squares), natural Atacama  $\text{ClO}_4^-$  (open blue circles and closed blue circles for actual fertilizer samples), and synthetic  $\text{ClO}_4^-$  (open black circles).

## **List of Tables**

- Table 3.1. Perchlorate concentrations and Cl and O isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.
- Table 3.2. Isotopic compositions of hypothetical endmembers used for analysis of dominant sources in Study Area groundwater.
- Table 3.3. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $\delta^{37}\text{Cl}$  vs  $\delta^{18}\text{O}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.
- Table 3.4. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $\Delta^{17}\text{O}$  vs  $\delta^{18}\text{O}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.
- Table 3.5. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $^{36}\text{Cl}/\text{Cl}$  abundance vs  $\delta^{37}\text{Cl}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.
- Table 3.6. Perchlorate Cl and O isotope data for replicate sample columns from wells in the Study Area, June 2010 to February 2012.
- Table 3.7. Perchlorate isotope data using three different methods of O stable isotope analysis for samples collected from wells in the Study Area, June 2010 to February 2012.



## List of Acronyms and Abbreviations

‰	per mil
$\delta$ , $\Delta$	delta, relative difference of isotope ratios
Ag	silver
AgCl	silver chloride
AgNO <sub>3</sub>	silver nitrate
AMS	accelerator mass spectrometry
BaSO <sub>4</sub>	barium sulfate
bls	below land surface
C	carbon
<sup>12</sup> C	carbon-12
<sup>13</sup> C	carbon-13
°C	degrees Celsius
CB&I	CB&I Federal Services, LLC
CF	continuous-flow
CF-IRMS	continuous-flow isotope ratio mass spectrometry
CH <sub>3</sub> Cl	methyl chloride
CH <sub>3</sub> I	methyl iodide
Cl <sup>-</sup>	chloride
Cl	chlorine
<sup>35</sup> Cl	chlorine-35
<sup>36</sup> Cl	chlorine-36
<sup>37</sup> Cl	chlorine-37
ClO <sub>3</sub> <sup>-</sup>	chlorate
ClO <sub>4</sub> <sup>-</sup>	perchlorate
cm	centimeters
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
DI	dual-inlet
DI-IRMS	dual-inlet isotope ratio mass spectrometry
DIW	deionized water
DO	dissolved oxygen
DoD	Department of Defense
EIGL	Environmental Isotope Geochemistry Laboratory
ESTCP	Environmental Security Technology Certification Program
Fe	iron
Fe <sup>3+</sup>	Iron (III)
FeCl <sub>3</sub>	iron (III) chloride
FeCl <sub>4</sub> <sup>-</sup>	tetrachloroferrate
GIS	geographic information system
<sup>2</sup> H	deuterium
<sup>3</sup> H	tritium
HCl	hydrochloric acid

HCO <sub>3</sub> <sup>-</sup>	bicarbonate
He	helium
HNO <sub>3</sub>	nitric acid
H <sub>2</sub> O	water
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
hr	hours
IAEA	International Atomic Energy Agency
IC	ion chromatography
IRMS	isotope-ratio mass-spectrometry
ITRC	Interstate Technology & Regulatory Council
IX	ion exchange
k	one thousand
KCl	potassium chloride
KClO <sub>4</sub>	potassium perchlorate
kg	kilogram
km <sup>2</sup>	square kilometer
KNO <sub>3</sub>	potassium nitrate
KOH	potassium hydroxide
L	liter
LPM	liters per minute
µg	microgram
µg/L	microgram per liter
µmol	micromole
M	molar
MΩ	megaohm
MADEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
mg	milligram
mL	milliliter
mm	millimeter
MRGB	Middle Rio Grande Basin
MVSL	Mid-Valley Sanitary Landfill
<i>m/z</i>	mass to charge ratio
N	nitrogen or normal or number of entities
N <sub>2</sub>	nitrogen gas
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
NaNO <sub>3</sub>	sodium nitrate
ng	nanogram
NH <sub>4</sub> ClO <sub>4</sub>	ammonium perchlorate
N <sub>2</sub>	nitrogen gas
NO <sub>2</sub>	nitrogen dioxide
NO <sub>3</sub> <sup>-</sup>	nitrate
NWIS	National Water Information System
O	oxygen
<sup>16</sup> O	oxygen-16

$^{17}\text{O}$	oxygen-17
$^{18}\text{O}$	oxygen-18
$\text{O}_2$	oxygen gas
$\text{O}_3$	ozone
pCi	picoCuries
pCi/L	picoCuries per liter
per mil (‰)	part per thousand ( $\times 10^{-3}$ )
PRIME	Purdue Rare Isotope Measurement Laboratory
QA/QC	Quality Assurance/Quality Control
<i>R</i>	ratio
RFF	rockets, fireworks, and flares
rg	reference gas
S	sulfur
SARWQCB	Santa Ana Regional Water Quality Control Board
SERDP	Strategic Environmental Research and Development Program
SHP	Southern High Plains
SIMS	secondary ion mass spectrometry
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
$\text{SO}_4^{2-}$	sulfate
TAC	Technical Advisory Committee
TPA	tetrapentylammonium
TPABr	tetrapentylammonium bromide
TPAClO <sub>4</sub>	tetrapentylammonium perchlorate
UIC	University of Illinois at Chicago
U.S.	United States
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
wt	weight
yr	year

## Abstract

Perchlorate ( $\text{ClO}_4^-$ ) in groundwater can be from synthetic or natural sources, the latter of which include both historical application of imported nitrate fertilizers from the Atacama Desert of Chile and naturally deposited  $\text{ClO}_4^-$  that forms atmospherically and accumulates in arid regions such as the southwestern US. The objective of this study was to evaluate the use of isotopic data to distinguish sources of  $\text{ClO}_4^-$  in groundwater in a specific region of the Rialto-Colton and Chino, CA groundwater subbasins (Study Area). This region includes two groundwater  $\text{ClO}_4^-$  plumes emanating from known military/industrial source areas, and a larger area outside of these plumes having measurable  $\text{ClO}_4^-$ . Perchlorate extracted from wells in this region was analyzed for chlorine and oxygen stable isotope ratios ( $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ) and radioactive chlorine-36 ( $^{36}\text{Cl}$ ) isotopic abundance, along with other geochemical, isotopic, and hydrogeologic data. Isotope data indicate synthetic, Atacama, and indigenous natural  $\text{ClO}_4^-$  were present in the Study Area. Stable isotope data from nearly all sampled wells within the contours of the two characterized plumes, including those located in a perched zone and within the regional groundwater aquifer, were consistent with a dominant synthetic  $\text{ClO}_4^-$  source. In wells downgradient from the synthetic plumes and in the Chino subbasin to the southwest, isotopic data indicate the dominant source of  $\text{ClO}_4^-$  largely was Atacama, presumably from historical application of nitrate fertilizer in this region. Past agricultural land use and historical records are consistent with this source being present in groundwater. The  $^{36}\text{Cl}$  and  $\delta^{18}\text{O}$  data indicate that wells having predominantly synthetic or Atacama  $\text{ClO}_4^-$  also commonly contained small fractions of indigenous natural  $\text{ClO}_4^-$ . The indigenous  $\text{ClO}_4^-$  was most evident isotopically in wells having the lowest overall  $\text{ClO}_4^-$  concentrations ( $< 1 \mu\text{g/L}$ ), consistent with its occurrence as a low-level background constituent in the region. A small subset of wells outside the contours of the two synthetic plumes, including an upgradient well, had characteristics indicating small amounts of synthetic  $\text{ClO}_4^-$  mixed with one or both of the natural source types. Hydrogeologic data indicate synthetic  $\text{ClO}_4^-$  in the upgradient well may be from a source other than the identified plume sources, but it is not known whether this source might also be present in other wells at low concentrations. The stable isotope and  $^{36}\text{Cl}$  data provided relatively unambiguous discrimination of synthetic and Atacama  $\text{ClO}_4^-$  sources

in most wells having relatively high concentrations, providing regional perspective on anthropogenic  $\text{ClO}_4^-$  contamination in the Rialto-Colton and Chino subbasins. Where indigenous natural  $\text{ClO}_4^-$  was indicated as a substantial component, total  $\text{ClO}_4^-$  concentrations were low and concentrations of anthropogenic components were near background levels.

## 1.0 Introduction

The contamination of groundwater in the United States by perchlorate ( $\text{ClO}_4^-$ ) has become an issue of national concern. It was once assumed that  $\text{ClO}_4^-$  contamination of groundwater largely resulted from historical testing and disposal practices by the military, the aerospace and ordnance industries, and  $\text{ClO}_4^-$  manufacturers. However, during the past decade it has become apparent that widespread agricultural use of nitrate fertilizer from the Atacama Desert of Chile (Urbansky et al., 2001a,b; Böhlke et al., 2005; Böhlke et al., 2009; Sturchio et al., 2011, 2012, 2014) as well as mobilization of indigenous natural  $\text{ClO}_4^-$  (Dasgupta et al., 2005, 2006; Rao et al., 2007) may also contribute to groundwater contamination. Isotopic techniques have been developed over the past decade to characterize different sources of  $\text{ClO}_4^-$  in the environment. The objective of this study was to evaluate sources of  $\text{ClO}_4^-$  in groundwater in a specific region of the Rialto-Colton and Chino, CA subbasins (Study Area) using chlorine and oxygen stable isotope ratio analysis and chlorine-36 ( $^{36}\text{Cl}$ ) radioactive isotope analysis. In conjunction with  $\text{ClO}_4^-$  isotopic analysis, additional geochemical and hydrogeological data were collected in this region and evaluated. This evaluation included (1) water level mapping to evaluate the flow of groundwater, and the potential for  $\text{ClO}_4^-$  transport in the study area; (2) water chemistry analyses, including major ion composition,  $\text{ClO}_4^-$  concentrations, stable isotope ratios of hydrogen, oxygen, nitrogen, and sulfur in water, nitrate, and sulfate, groundwater age dating parameters, and dissolved gases; and (3) coupled well-bore flow and depth-dependent water quality data for several groundwater supply wells. The geochemical and hydrogeological data, along with interpretations, were published previously (Izbicki et al., 2014). That paper provides the hydrogeologic framework to support the isotopic study described herein.

### 1.1 Perchlorate Sources

The following sections summarize information about the principal sources of  $\text{ClO}_4^-$  in the environment.

### 1.1.1 Synthetic Perchlorate

Ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) has been used for several decades in the United States (U.S.) as the primary oxidant in a variety of solid rocket propellants and explosives produced for military and aerospace applications. More than 100 varieties of military rocket motors contain  $\text{NH}_4\text{ClO}_4$  (Cunniff et al., 2006). Potassium perchlorate ( $\text{KClO}_4$ ) is also used for many military applications. Besides military propellants and explosives, a variety of commercial products contain synthetic  $\text{ClO}_4^-$  either intentionally or as a manufacturing byproduct, including fireworks, matches, air bags, chlorine bleach, safety flares, perchloric acid, and chlorate herbicides (Trumpholt et al., 2005; Aziz et al., 2006, 2008).

Based on United States Environmental Protection Agency (USEPA) estimates, approximately  $4 \times 10^8$  kg (400,000 metric tons) of synthetic  $\text{ClO}_4^-$  has been produced in the U.S. since the 1950's, with an average production rate of  $7.1 \times 10^6$  kg/yr from 1951-1997 (Dasgupta et al., 2006). Historical testing and disposal practices at some military installations,  $\text{ClO}_4^-$  production facilities, and aerospace sites have resulted in substantial contamination of soils and groundwater at these locations. Many groundwater plumes, which are often extensive and have  $\text{ClO}_4^-$  concentrations up to several hundred milligrams per liter (mg/L), have been identified and are subject to site assessment and(or) remediation (e.g., Hatzinger, 2005; ITRC, 2008). However, the contribution of other commercial products as non-point or small point sources of synthetic  $\text{ClO}_4^-$  is more difficult to assess and quantify, although road flares, blasting agents, and fireworks have been indicated as sources of  $\text{ClO}_4^-$  in some groundwaters (e.g., MADEP, 2007; Munster et al., 2008; Munster, 2008; Böhlke et al., 2009; Munster and Hanson, 2009). Further information on synthetic  $\text{ClO}_4^-$  sources can be found in previously published reviews (Trumpholt et al., 2005; ITRC, 2008; Aziz et al., 2006).

### 1.1.2 Atacama Nitrate Deposits and Fertilizer

Natural  $\text{ClO}_4^-$  has long been known to co-occur with sodium nitrate ( $\text{NaNO}_3$ ) in surficial deposits in the Atacama Desert of Chile at an average concentration of around 0.1 % (by mass) of the total soluble salt, with concentrations as high as 6.8 % reported (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2006). These  $\text{NO}_3^-$  deposits,

sometimes referred to as “nitrate caliche”, were widely used in the U.S. during the first half of the 20<sup>th</sup> century as a source of inorganic nitrogen fertilizer. According to the California Department of Agriculture, more than 477,000 metric tons of imported Atacama NO<sub>3</sub><sup>-</sup> was used in California as fertilizer between 1923 and 1998 (California Department of Food and Agriculture, 1999). The final ClO<sub>4</sub><sup>-</sup> concentration of processed Atacama NO<sub>3</sub><sup>-</sup> fertilizer prior to 2002 was variable, and likely ranged from ~1,500 to 10,000 mg/kg (i.e., 0.15 to 1.0 wt. %) based upon analysis of historical samples (Eldridge et al., 2000; Urbansky et al., 2001a,b; Dasgupta et al., 2006). Changes in manufacturing processes after 2002 were reported to reduce the final ClO<sub>4</sub><sup>-</sup> concentration to ≤ 100 mg/kg (0.01%) (Dasgupta et al., 2006). Thus, apart from synthetic sources, past application of Atacama NO<sub>3</sub><sup>-</sup> fertilizer provides a potential source of ClO<sub>4</sub><sup>-</sup> in groundwater and drinking water in the U.S.

Based on a reasonable assumption of ~2,000 mg ClO<sub>4</sub><sup>-</sup>/kg Atacama fertilizer (0.2%) (Dasgupta et al., 2006), one metric ton of processed Atacama fertilizer (prior to 2002) contained about 2 kg of ClO<sub>4</sub><sup>-</sup>; enough to contaminate more than 300 million liters of groundwater to above the current California maximum contaminant level (MCL) of 6 µg/L, assuming no losses to biodegradation or other removal processes. Additional information on Atacama NO<sub>3</sub><sup>-</sup> fertilizers as a source of ClO<sub>4</sub><sup>-</sup> can be found in published papers (Ericksen, 1981, 1983; Bao and Gu, 2004; Dasgupta et al., 2006; Jackson et al., 2006; Böhlke et al., 2009; Sturchio et al., 2011, 2012, 2014). Some other fertilizer materials, including plant products such as kelp, have been reported to contain ClO<sub>4</sub><sup>-</sup>, but the concentrations in these materials are generally orders of magnitude lower than those historically present in Atacama NO<sub>3</sub><sup>-</sup>, and they are considered less likely to be of widespread environmental significance (Dasgupta et al., 2006; Böhlke et al., 2009).

### 1.1.3 Indigenous Natural Perchlorate in the US

Natural ClO<sub>4</sub><sup>-</sup> that is not associated with fertilizers from the Atacama has also been detected in soils, groundwaters, and mineral deposits collected from arid regions in the western U.S., including groundwater underlying an area of 155,000 km<sup>2</sup> in the Southern High Plains (SHP) of Texas and New Mexico (Jackson et al., 2004, 2005, 2006; Dasgupta et al., 2005; Rajagopalan et al., 2006), in the Middle Rio Grande Basin of New



Mexico (Plummer et al., 2006), and also in the northwestern U.S. (Hatzinger et al., 2013). Natural  $\text{ClO}_4^-$  also was reported in the Great Lakes (Poghosyan et al., 2014). Based on groundwater dating, some New Mexico samples (having  $\text{ClO}_4^-$  concentrations ranging from  $\sim 0.12$  to  $1.8 \mu\text{g/L}$ ) were recharged many thousands of years before present, indicating pre-anthropogenic (natural)  $\text{ClO}_4^-$  sources and accumulation processes (Plummer et al., 2006). Natural  $\text{ClO}_4^-$  is hypothesized to form in the atmosphere through photochemical reactions (Murphy and Thomson, 2000; Bao and Gu, 2004; Dasgupta et al., 2005; Kang et al., 2008; Sturchio et al., 2009) and to reach Earth's surface via precipitation or dry deposition. This hypothesis was supported by ubiquitous occurrence of  $\text{ClO}_4^-$  in precipitation from National Atmospheric Deposition Program (NADP) collectors at 26 sites across the contiguous U.S., Puerto Rico, and Alaska over a 3-yr period at concentrations ranging from  $<5 \text{ ng/L}$  to  $102 \text{ ng/L}$  ( $n=1578$ ) (Rajagopalan et al., 2009).

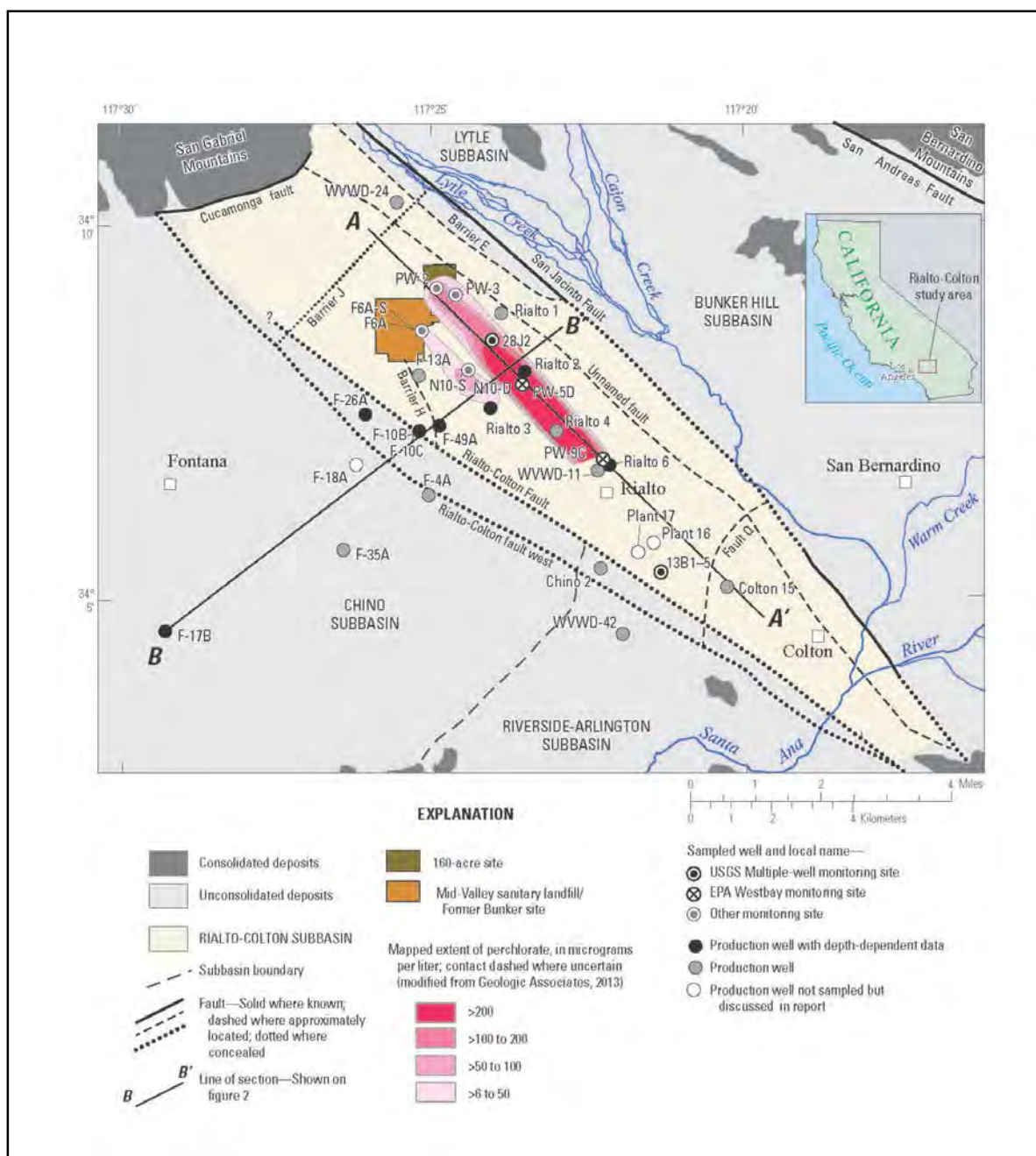
In arid regions, such as parts of the southwestern U.S.,  $\text{ClO}_4^-$  in wet and dry deposition can accumulate with time in the vadose zone, along with other deposited salts. Rao et al. (2007) detected  $\text{ClO}_4^-$  in the vadose zone at several sites in the southwestern U.S. with an average accumulated mass per unit area of  $408 \pm 88 \text{ g/ha}$ . The  $\text{ClO}_4^-$  concentrations were correlated ( $r = 0.59\text{-}0.99$ ) with those of meteoric  $\text{Cl}^-$  accumulated over the last 6 to 100 kyr, indicating that these anions accumulated together via similar processes. Indigenous natural  $\text{ClO}_4^-$  also is associated with natural surficial  $\text{NO}_3^-$  deposits in the vicinity of Death Valley, California at concentrations ranging from  $0.25$  to  $23 \text{ mg/kg}$  (Jackson et al., 2010; Lybrand et al., 2013). Similarly,  $\text{ClO}_4^-$  concentrations as high as  $1.1 \text{ mg/kg}$  were reported in surficial deposits in the Dry Valleys region of Antarctica (Kounaves et al., 2010; Jackson et al., 2013).

When unsaturated-zone salt accumulations in arid environments become subject to large-scale irrigation, such as in the SHP and other agricultural regions of the western U.S., accumulated  $\text{ClO}_4^-$  can be mobilized and transported to the water table. Such agricultural mobilization is hypothesized to account for high  $\text{ClO}_4^-$  concentrations in groundwater in West Texas, which has been widely irrigated for several decades for production of cotton and other crops (Rajagopalan et al., 2006). Irrigation also may be

associated with transport of  $\text{ClO}_4^-$  to groundwater from crops treated with Atacama nitrate fertilizer (Böhlke et al., 2009; Sturchio et al., 2014)

## **1.2 Location and Characteristics of the Study Area**

Release of synthetic  $\text{ClO}_4^-$  from military and industrial sources in the northern region of the Rialto-Colton subbasin of San Bernardino County, CA has impacted a number of municipal supply wells. Previously identified sources include two sites: (1) a 160-acre industrial site formerly occupied by several different industries, and also known as the “Rockets, Fireworks, and Flares” (RFF) site (USEPA, 2014), and (2) properties adjacent to the current Mid-Valley Sanitary Landfill (MVSL) operated by San Bernardino County, including the Rialto Ammunition Backup Storage Point, a site of several World War II era bunkers that were later used for the manufacture, transport, and/or disposal of fireworks, flares, explosives and other potentially hazardous materials (SAIC, 2004). This site is known as the “Mid Valley Sanitary Landfill/Bunker Site” (Geologic Associates, 2003; SARWQCB, 2005; Woolfenden, 2007) or the “Former Bunker Area”. The distribution of  $\text{ClO}_4^-$  concentrations in wells indicates two parallel plumes emanating from those sites (Figure 1.1). As defined by previous studies, the mapped plume from the 160-acre site is parallel to the Rialto-Colton fault and extends at least 6 km downgradient of the site in the southeast direction of groundwater flow (GeoLogic Associates, 2013). Recent USEPA reports suggest that this plume may reach as far as 9 km downgradient, but the distal extent is not yet known (USEPA, 2014). The mapped plume from the Bunker Site/MVSL extends ~ 3 km downgradient, parallel to the RFF site plume.



**Figure 1.1. Overhead view of the Study Area with the two previously identified source areas and the associated perchlorate plumes delineated.** Figure from Izbicki et al. (2014). This plume map was generated previously and modified from Geologic Associates (2013). The map does not include concentration data from this study, the most recent USEPA site sampling (USEPA, 2014) or Izbicki et al. (2014).

The extent of high-level  $\text{ClO}_4^-$  contamination (e.g.,  $> 50 \text{ } \mu\text{g/L}$ ) emanating as plumes from the two military/industrial sites is reasonably well defined. However,  $\text{ClO}_4^-$  has also been detected in groundwater wells throughout the Study Area at lower concentrations ( $\sim 1$  to  $20 \text{ } \mu\text{g/L}$ ). Perchlorate has been measured in groundwater wells to the southeast of the two known plumes in the general direction of groundwater flow, such as Colton 15 and 13B1-5 (RHSW-5), and in wells to the south of the sources but outside the hypothesized groundwater flow path, including a number of wells positioned to the south of the Rialto-Colton Fault in the Chino subbasin, such as F-35A, F-4A, F-17B and others (Figure 1.1). Several wells in the Chino subbasin positioned between the Rialto-Colton Fault and the postulated Rialto-Colton Fault West (Paulinski, 2012), such as F-26A and Chino 2 (Figure 1.1), also have measurable  $\text{ClO}_4^-$ , albeit at very low concentrations ( $< 2 \text{ } \mu\text{g/L}$ ). The general pattern of low-level  $\text{ClO}_4^-$  contamination in groundwater throughout the Study Area (apart from the plumes emanating from the two source areas) suggests the possibility of additional sources of  $\text{ClO}_4^-$  in the area, possibly including  $\text{ClO}_4^-$  derived from historical Atacama fertilizer application, natural indigenous  $\text{ClO}_4^-$ , and secondary synthetic sources from flares, fireworks, blasting, or others. The focus of this project was to use stable isotope ratio analysis and  $^{36}\text{Cl}$  analysis to evaluate the major source(s) of  $\text{ClO}_4^-$  throughout the Study Area. A separate report provides information on groundwater flow and additional hydrogeochemical characteristics in the Study Area (Izbicki et al., 2014).

### 1.3 Isotopic Analyses of $\text{ClO}_4^-$

The two elements comprising the  $\text{ClO}_4^-$  molecule (i.e., Cl and O) each have multiple stable isotopes. Oxygen has three stable isotopes ( $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ ), which have molar abundances (mole fractions) of approximately 99.8 %, 0.04 %, and 0.20 %, respectively (Coplen et al., 2002). Chlorine has two stable isotopes ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ), with molar abundances of approximately 75.8 % and 24.2 %, respectively (Coplen et al., 2002).

Stable isotopic compositions are measured and reported as relative differences of isotope ratios (in either moles or numbers of atoms) between two substances, one of which is generally an international measurement standard. For oxygen:

$$[\text{Eq. 1.1}] \quad \delta^{18}\text{O} = R(^{18}\text{O}/^{16}\text{O})_{\text{sample}}/R(^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1$$

$$[\text{Eq. 1.2}] \quad \delta^{17}\text{O} = R(^{17}\text{O}/^{16}\text{O})_{\text{sample}}/R(^{17}\text{O}/^{16}\text{O})_{\text{standard}} - 1,$$

where the standard in both equations is Vienna Standard Mean Ocean Water (VSMOW).  $R$  = molar ratio. Values of  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  are reported in parts per thousand (per mil, or ‰). By international convention, the  $\delta^{18}\text{O}$  scale is defined by two reference materials, with VSMOW at 0.0 ‰ and Standard Light Antarctic Precipitation (SLAP) at a value of -55.5 ‰ (Gonfiantini, 1978; Coplen, 1994).

Variations in  $R(^{17}\text{O}/^{16}\text{O})$  and  $R(^{18}\text{O}/^{16}\text{O})$  caused by most physical-chemical fractionation processes on Earth are related systematically by the relative differences in the masses of the isotopes. Such “mass-dependent” variations can vary slightly for different processes and they can be described in various ways (e.g., Thiemens, 1999; Miller, 2002; Angert et al., 2004; Assonov and Brenninkmeijer, 2005). For this project:

$$[\text{Eq. 1.3}] \quad (1 + \delta^{17}\text{O}) = (1 + \delta^{18}\text{O})^\lambda,$$

with  $\lambda \approx 0.525$  (Miller, 2002; Böhlke et al., 2005). Departures from mass-dependent O-isotope variation are important features of some materials, including some natural  $\text{ClO}_4^-$ . Departures from mass-dependent O-isotope variation in  $\text{ClO}_4^-$  are described in this report as deviations from the relation given in Equation 1.3:

$$[\text{Eq. 1.4}] \quad \Delta^{17}\text{O} = [(1 + \delta^{17}\text{O}) / (1 + \delta^{18}\text{O})^{0.525}] - 1.$$

Values of  $\Delta^{17}\text{O}$  are reported in parts per thousand (per mil, or ‰). Alternative definitions of  $\Delta^{17}\text{O}$  used to describe  $\text{ClO}_4^-$  isotope data can yield slightly different  $\Delta^{17}\text{O}$  values for the same measured  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values; those differences range from about 0.0 to 0.2 ‰ for groundwater data summarized in this report.

For reporting chlorine stable isotope ratios:

$$[\text{Eq. 1.5}] \quad \delta^{37}\text{Cl} = R(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} / R(^{37}\text{Cl}/^{35}\text{Cl})_{\text{standard}} - 1$$

where the international measurement standard is Standard Mean Ocean Chloride (SMOC). Values of  $\delta^{37}\text{Cl}$  typically are reported in parts per thousand (per mil, or ‰).

Chlorine also has a long-lived radioactive isotope ( $^{36}\text{Cl}$ ) with a half-life of  $\sim 301,000$  yr. The relative abundance of  $^{36}\text{Cl}$  is small (typically  $<10^{-15}$  to  $10^{-12}$  relative to the stable Cl isotopes) but it can be useful for studying origins of chloride and Cl-bearing compounds (Phillips, 2000). Techniques to analyze the stable isotopes of both chlorine and oxygen in the  $\text{ClO}_4^-$  molecule, as well as its  $^{36}\text{Cl}$  isotopic abundance, have been developed and used to characterize a variety of natural and man-made  $\text{ClO}_4^-$  samples, including Atacama nitrate fertilizers and caliche deposits, a wide array of synthetic  $\text{ClO}_4^-$  types and  $\text{ClO}_4^-$ -containing products (e.g., laboratory reagents, fireworks, flares, gunpowder, military sources), and samples from the southwest US that contain natural indigenous  $\text{ClO}_4^-$  (Bao and Gu, 2004; Böhlke et al., 2005, 2009; Jackson et al., 2010; Gu et al., 2011; Sturchio et al., 2006, 2009, 2012; Hatzinger et al., 2011, 2013). A summary of these techniques as applied to  $\text{ClO}_4^-$  isotopic analysis of Study Area groundwater samples is provided in Section 2.

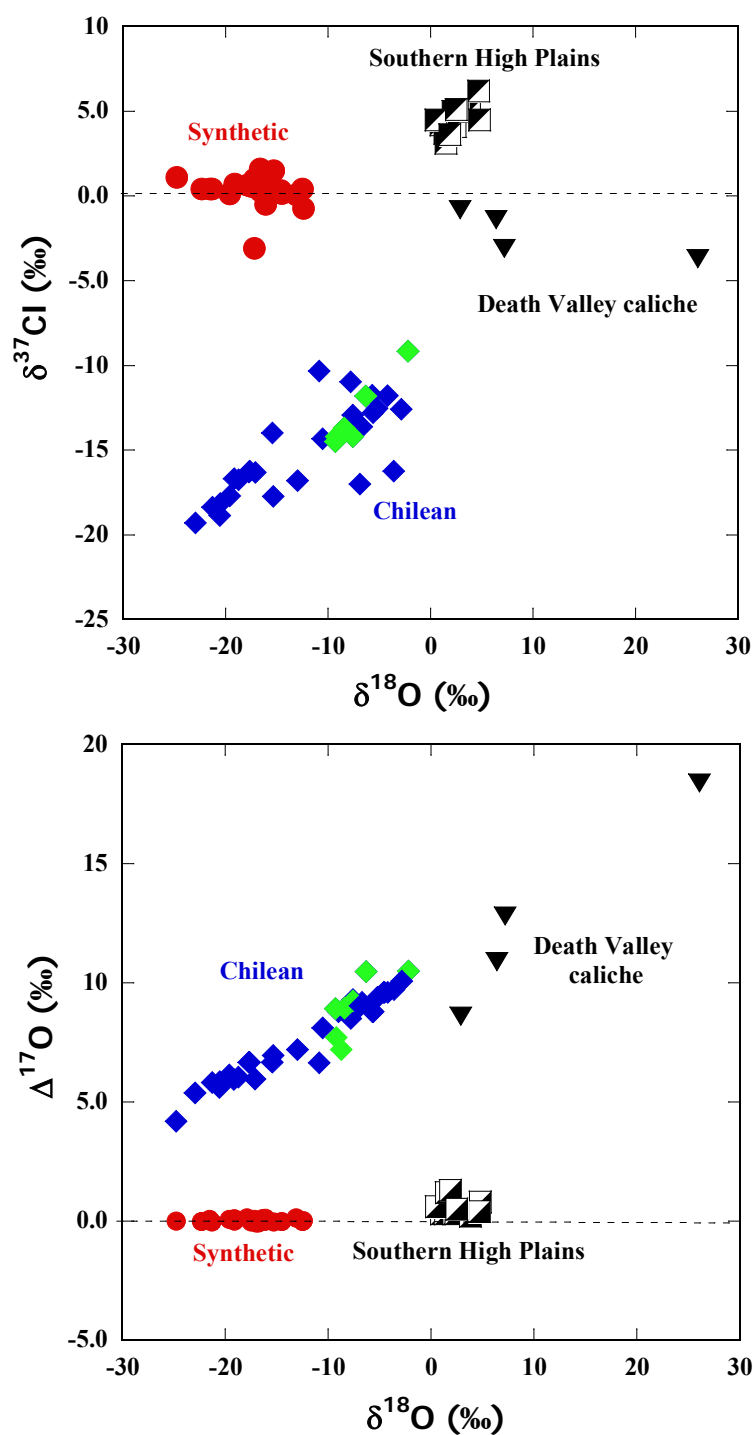
#### 1.3.1 Stable Isotope Ratios of Cl and O in Synthetic $\text{ClO}_4^-$

Synthetic  $\text{ClO}_4^-$  is synthesized electrochemically using NaCl and  $\text{H}_2\text{O}$  (Schumacher, 1960). Samples from a variety of different synthetic sources, including laboratory reagents, commercial manufacturers, and  $\text{ClO}_4^-$  derived from road flares, fireworks, Pyrodex gunpowder, and chlorate herbicides, were analyzed for Cl and O stable isotope ratios. Additional details on these samples are provided in Bao and Gu (2004), Böhlke et al. (2005), Sturchio et al. (2006, 2011), and Hatzinger et al. (2011, 2013). The  $\delta^{37}\text{Cl}$  values of all synthetic  $\text{ClO}_4^-$  samples published to date group within a range from  $-3$  ‰ to  $+2$  ‰. These values are similar to those reported for common industrial sources of NaCl, such as halite from Phanerozoic bedded marine evaporites, which has a mean  $\delta^{37}\text{Cl}$  value of  $0.0 \pm 0.9$  ‰ (Eastoe et al., 2007). The electrochemical synthesis of  $\text{ClO}_4^-$  is nearly stoichiometric for  $\text{Cl}^-$  (i.e., nearly all of the added  $\text{Cl}^-$  is converted to  $\text{ClO}_4^-$ ), so the Cl isotope ratio in the  $\text{ClO}_4^-$  product is similar to that in the starting NaCl. The published  $\delta^{18}\text{O}$  values of synthetic  $\text{ClO}_4^-$  vary over a wider range than those for  $\delta^{37}\text{Cl}$ , from  $-25$  ‰

to -13 ‰ (Figure 1.2). It has been hypothesized that the  $\delta^{18}\text{O}$  values of the synthetic  $\text{ClO}_4^-$  samples generally reflect the  $\delta^{18}\text{O}$  in the  $\text{H}_2\text{O}$  used for production modified by O isotopic fractionation during  $\text{ClO}_4^-$  synthesis (Sturchio et al., 2006). In contrast to  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  values of all synthetic  $\text{ClO}_4^-$  samples analyzed to date are indistinguishable ( $0.0 \pm 0.1$  ‰), indicating that there is negligible mass-independent isotopic fractionation of O during  $\text{ClO}_4^-$  synthesis (Sturchio et al., 2006).

### 1.3.2 Stable Isotope Ratios of Cl and O in Atacama $\text{ClO}_4^-$

Current data from isotopic analyses reveal that the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope ratio ( $\delta^{37}\text{Cl}$  value) of naturally-occurring  $\text{ClO}_4^-$  from Chile is consistently and significantly lower than that of synthetic  $\text{ClO}_4^-$  from all other sources tested (Figure 1.2). In fact, the reported  $\delta^{37}\text{Cl}$  values for Atacama  $\text{ClO}_4^-$  are the lowest for any common substance on Earth (Coplen et al., 2002). Based on samples analyzed to date, which include soils, caliche deposits and a groundwater sample from the Atacama Desert (blue diamonds in Figure 1.2), and samples of commercial Atacama nitrate fertilizer (green diamonds in Figure 1.2), the  $\delta^{37}\text{Cl}$  values range from -19 to -9 ‰ (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006, 2012; Böhlke et al., 2009; Jackson et al., 2010; Hatzinger et al., 2011, 2013; unpublished results from SERDP Project ER-1435 for a subset of the Atacama soil samples). The  $^{18}\text{O}/^{16}\text{O}$  isotope ratio ( $\delta^{18}\text{O}$  value) of Atacama natural  $\text{ClO}_4^-$  spans a wide range, from -25 to -2 ‰, which overlaps that of synthetic  $\text{ClO}_4^-$  (Figure 1.2).



**Figure 1.2.** Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in natural indigenous  $\text{ClO}_4^-$  of the US Southern High Plains (black and white squares) and Death Valley caliche (black triangles), natural Atacama  $\text{ClO}_4^-$ , (blue diamonds for caliche and groundwater and green diamonds for nitrate fertilizer samples) and synthetic  $\text{ClO}_4^-$  (red circles). Sources of data are provided in the accompanying text.



One important isotopic difference between synthetic  $\text{ClO}_4^-$  and natural  $\text{ClO}_4^-$  from the Atacama Desert is revealed by analysis of  $^{17}\text{O}$  abundances. Synthetic  $\text{ClO}_4^-$  samples have  $\Delta^{17}\text{O}$  values near 0, consistent with  $\text{ClO}_4^-$  production from brine by electrolysis. In contrast,  $\Delta^{17}\text{O}$  values of Atacama  $\text{ClO}_4^-$  samples analyzed to date range from + 4 to +11 ‰, with commercial nitrate fertilizer  $\text{ClO}_4^-$  samples being in the upper end of this range (Figure 1.2). Elevated  $\Delta^{17}\text{O}$  values in Atacama  $\text{ClO}_4^-$  were first measured by Bao and Gu (2004), who noted that the  $^{17}\text{O}$  enrichment is consistent with an atmospheric formation mechanism. The data indicate that oxidation of volatile Cl species by ozone ( $\text{O}_3$ ) (which is known to have elevated  $\Delta^{17}\text{O}$  values; Johnson et al., 2000) in the upper atmosphere may be responsible for the initial production of this  $\text{ClO}_4^-$  (Bao and Gu, 2004; Rao et al., 2010).

### 1.3.3 Stable Isotope Ratios of Cl and O in Indigenous Natural $\text{ClO}_4^-$

As previously discussed, research conducted during the past decade has revealed that natural  $\text{ClO}_4^-$  occurs in environments other than the Atacama Desert of Chile. Most significantly for forensic studies in the U.S., indigenous natural  $\text{ClO}_4^-$  has been widely detected in the southwestern U.S., as evidenced through various surveys of  $\text{ClO}_4^-$  in surface soils, vadose-zone profiles, wet and dry deposition, and groundwater in New Mexico, Texas, California and elsewhere in this region (Dasgupta et al., 2006; Plummer et al., 2006; Rajagopalan et al., 2006, 2009; Rao et al., 2007; Parker et al., 2008; Jackson et al., 2010; Lybrand et al., 2013). Recent detections of  $\text{ClO}_4^-$  in Antarctic dry valley soils and lakes, and also on the surface of Mars, have caused additional interest in natural  $\text{ClO}_4^-$  (Hecht et al. 2009; Ming et al. 2010; Catling et al. 2010; Kounaves et al. 2010; Jackson et al., 2013).

The stable isotopic composition of indigenous natural  $\text{ClO}_4^-$  from several locations and environments (vadose zone, surface caliche deposits, groundwater) in the southwestern U.S. has recently been reported (Jackson et al., 2010; Hatzinger et al., 2013). Groundwater  $\text{ClO}_4^-$  samples were obtained from the Southern High Plains (SHP; including one sample from the adjacent rolling plains) of western Texas and eastern New Mexico and from the Middle Rio Grande Basin (MRGB) of central New Mexico. A single sample was obtained from a natural subsurface accumulation of salts within

unsaturated sub-soils at the Range Ecology Research Site at Texas Tech University. Lastly,  $\text{ClO}_4^-$  was collected from near-surface caliche-type salt deposits on clay hills at four locations in the Death Valley region of the Mojave Desert, CA. Clay-hills caliche salts in this area were studied previously because of their unusually high  $\text{NO}_3^-$  concentrations, which resemble those in the Atacama Desert (Ericksen et al., 1983; Böhlke et al., 1997; Lybrand et al., 2013).

All of the indigenous samples collected from groundwater and vadose soils in the SHP and from groundwater in the MRGB were similar isotopically, despite the large areal extent over which they were collected, with  $\delta^{37}\text{Cl}$  values ranging from +3 to +5 ‰,  $\delta^{18}\text{O}$  values ranging from 0 to +4 ‰, and  $\Delta^{17}\text{O}$  values ranging from +0.3 to +1.3 ‰. The data indicate that  $\text{ClO}_4^-$  from the SHP and MRGB regions of Texas and New Mexico is consistently different from both Atacama  $\text{ClO}_4^-$  and synthetic  $\text{ClO}_4^-$  when all relevant stable isotopic abundances are considered ( $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) (Figure 1.2). Similar isotopic characteristics to those of the SHP and MRGB samples were also recently observed for presumably indigenous  $\text{ClO}_4^-$  from the U.S. Great Lakes (lake water) and from the Umatilla Basin, Oregon (groundwater), although the  $\Delta^{17}\text{O}$  values were slightly higher for some of these samples, ranging to +2.9 ‰ in Umatilla and +2.7 ‰ in the Great Lakes (Hatzinger et al., 2013; Poghosyan et al., 2014). The smaller, but significantly positive,  $\Delta^{17}\text{O}$  values of indigenous groundwater  $\text{ClO}_4^-$  in comparison to Atacama  $\text{ClO}_4^-$  could indicate either (1) indigenous groundwater  $\text{ClO}_4^-$  is formed predominantly by a different mechanism than Atacama  $\text{ClO}_4^-$  or (2) the indigenous  $\text{ClO}_4^-$  initially had higher  $\Delta^{17}\text{O}$  but was affected by post depositional O exchange with groundwater.

$\text{ClO}_4^-$  samples from the Death Valley caliche deposits, which have  $\text{ClO}_4^-$  concentrations ranging from 0.25 to 1.7 mg/kg (about 1-3 orders of magnitude lower than the Atacama deposits), have isotopic characteristics that differ from those of Atacama and synthetic  $\text{ClO}_4^-$ , and from those of SHP and MRGB samples. In comparison to the SHP samples, the Death Valley samples have lower  $\delta^{37}\text{Cl}$  values (from -0.8 to -3.7 ‰) and much higher  $\Delta^{17}\text{O}$  values (+8.6 to +18.4 ‰). As is apparent from Figure 1.2,  $\Delta^{17}\text{O}$  values of Death Valley samples are similar to or, in some instances, higher than those of the Atacama samples, consistent with an important component of atmospheric origin and

relative lack of post depositional exchange of O with groundwater. The SHP/MRGB and Death Valley samples can be considered together as “U.S. indigenous sources” and, even though there are substantial ranges in the individual isotope values, this indigenous grouping remains isotopically distinct from synthetic and Atacama  $\text{ClO}_4^-$ .

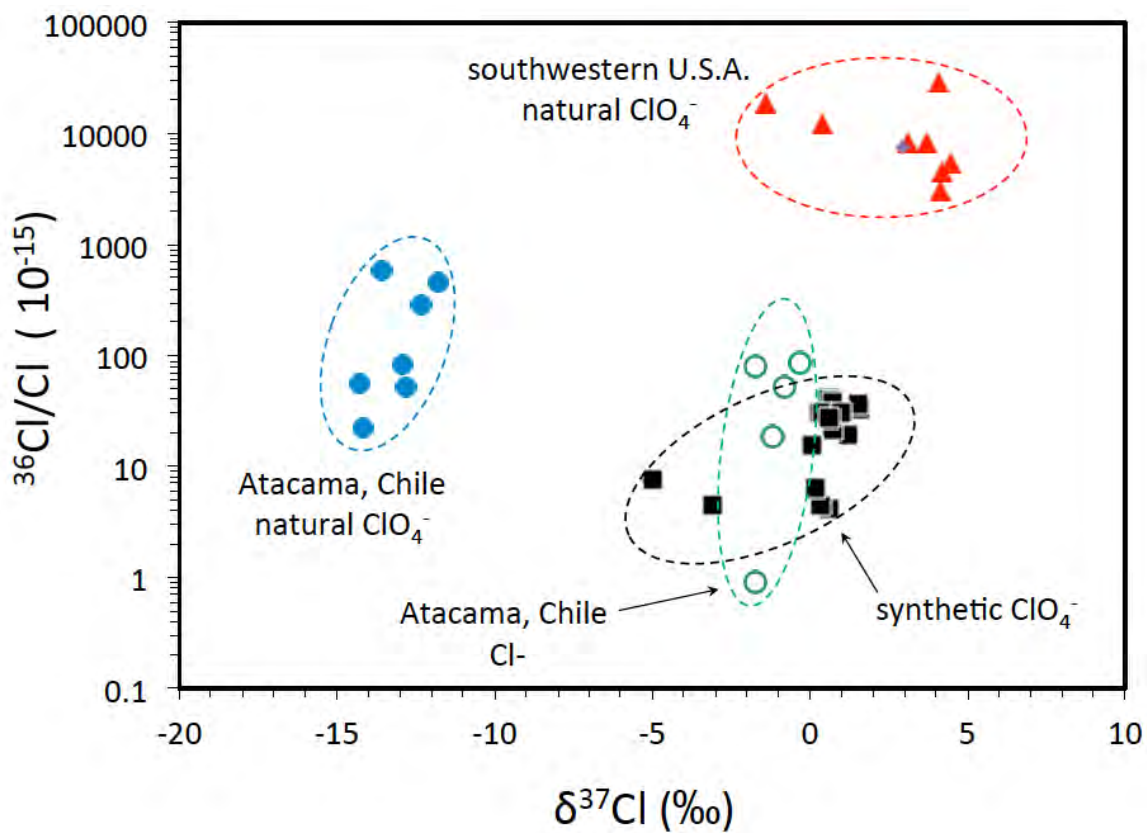
Given present data, it is not yet possible to fully explain the origin of the observed variations in the stable isotopic composition of natural  $\text{ClO}_4^-$  sources. The data permit the interpretation that natural  $\text{ClO}_4^-$  may have more than one formation mechanism, there may be global variations in the isotopic compositions of precursor compounds, and it may be subject to isotopic modification in the terrestrial environment. Resolving these issues would contribute to understanding atmospheric Cl chemistry, as well as the veracity of the isotopic approach for quantifying  $\text{ClO}_4^-$  sources in the environment. Nevertheless, despite uncertainty about processes responsible for some of the isotopic variations, it appears that natural  $\text{ClO}_4^-$  indigenous to the southwestern U.S. is distinguishable from synthetic  $\text{ClO}_4^-$  and from imported Atacama  $\text{ClO}_4^-$  on the basis of isotopic composition. These differences in isotopic composition may find important applications in resolving questions of  $\text{ClO}_4^-$  source apportionment for affected water supplies, such as those in the Study Area.

#### 1.4 Abundance of $^{36}\text{Cl}$ in Synthetic and Natural Perchlorate

The abundance of the radioactive isotope  $^{36}\text{Cl}$  (reported as atom fraction, or mole fraction, designated as  $^{36}\text{Cl}/\text{Cl}$ ) has proven to be another important tool for distinguishing  $\text{ClO}_4^-$  sources. Chlorine-36 is present naturally in  $\text{Cl}^-$  in groundwater in the U.S., with  $^{36}\text{Cl}/\text{Cl}$  values ranging from  $\sim 10 \times 10^{-15}$  near coasts to as high as  $\sim 1700 \times 10^{-15}$  in the central Rocky Mountains (Bentley et al., 1986; Phillips, 2000; Davis et al., 2003). Isotopic abundances of  $^{36}\text{Cl}$  measured in 35 different  $\text{ClO}_4^-$  samples from synthetic, Atacama, and southwestern U.S. sources ranged over more than four orders of magnitude (Figure 1.3 and Sturchio et al., 2009). Synthetic  $\text{ClO}_4^-$  samples were characterized by relatively low values of  $^{36}\text{Cl}/\text{Cl}$  from  $0 \times 10^{-15}$  to  $40 \times 10^{-15}$  (Sturchio et al., 2009). These values are consistent with  $\text{Cl}$  sources such as the geologically ancient halite-rich evaporite deposits (e.g., salt domes, bedded salts) from which large amounts of  $\text{NaCl}$  are mined commercially in the form of rock salt.

In contrast to synthetic samples, all indigenous natural  $\text{ClO}_4^-$  samples from the southwestern U.S. that were tested (including some of the SHP and MRGB groundwater samples and Death Valley deposits described in the previous section and shown in Figure 1.2 with differing  $\delta^{37}\text{Cl}$  and  $\Delta^{17}\text{O}$  values) had unusually high  $^{36}\text{Cl}/\text{Cl}$  values, ranging from  $3,130 \times 10^{-15}$  to  $28,800 \times 10^{-15}$ . Groundwater samples with indigenous  $\text{ClO}_4^-$  (and some with mixed indigenous/synthetic  $\text{ClO}_4^-$ ) from eastern Oregon similarly had elevated  $^{36}\text{Cl}/\text{Cl}$  values ( $4,530 - 15,900 \times 10^{-15}$ ; Hatzinger et al., 2011) as did samples collected from the U.S. Great Lakes, where the isotopic characteristics of  $\text{ClO}_4^-$  (which were similar to the southwestern U.S.) suggested a dominantly indigenous source ( $7,400 - 71,200 \times 10^{-15}$ ). The presence of bomb-generated  $^{36}\text{Cl}$  from nuclear tests in the mid 1950's (Phillips, 2000; Davis et al., 2003) could not be ruled out for samples from southwestern U.S. groundwater having detectable tritium, and apparently it is present in indigenous  $\text{ClO}_4^-$  in the upper Great Lakes, which still contain much of the water that was present in the 1950s and 1960s (Poghosyan et al., 2014). However,  $^{36}\text{Cl}/\text{Cl}$  values as high as  $8,400 \times 10^{-15}$  were measured in  $\text{ClO}_4^-$  from old groundwater in New Mexico with estimated recharge ages of  $> 5,000$  yr (Plummer et al., 2006; Sturchio et al., 2009). High concentrations of  $^{36}\text{Cl}$  in some  $\text{ClO}_4^-$  samples may point toward the stratosphere, rather than the troposphere, as an important area of atmospheric  $\text{ClO}_4^-$  formation (Sturchio et al., 2009).

Natural  $\text{ClO}_4^-$  from Atacama deposits had  $^{36}\text{Cl}/\text{Cl}$  ratios from  $22 \times 10^{-15}$  to  $590 \times 10^{-15}$ , much lower than any of the natural samples from the southwestern U.S., Great Lakes, or Umatilla area. The Atacama samples may have had higher initial  $^{36}\text{Cl}/\text{Cl}$  ratios that decreased via radioactive decay. This could be consistent with a relatively long history of Atacama  $\text{ClO}_4^-$  accumulation, as hyper-arid conditions in this region have persisted for at least 3 to 8 million years (Alpers and Brimhall, 1988; Hartley and Chong, 2002), which is 10 or more times the 301,000-yr half-life of  $^{36}\text{Cl}$ . The  $^{36}\text{Cl}/\text{Cl}$  ratios in  $\text{Cl}^-$  from the Atacama Desert are similar to those of the coexisting  $\text{ClO}_4^-$  as shown in Figure 1.3, which indicates that  $^{36}\text{Cl}$  in these samples may be near radioactive equilibrium with its environment. The accumulation time of  $\text{ClO}_4^-$  in the arid southwestern U.S. appears to have been much shorter (of the order of  $10^4$  yr) than that in the Atacama Desert, and natural  $\text{ClO}_4^-$  accumulated from the atmosphere during the past  $10^4$  years would still possess most of its initial  $^{36}\text{Cl}$  activity (Jackson et al., 2010). More importantly for forensic studies of  $\text{ClO}_4^-$ ,  $^{36}\text{Cl}$  abundances in combination with stable isotope ratios of O and Cl help differentiate synthetic, Atacama, and indigenous U.S.  $\text{ClO}_4^-$  sources (Sturchio et al., 2009; Hatzinger et al., 2011).



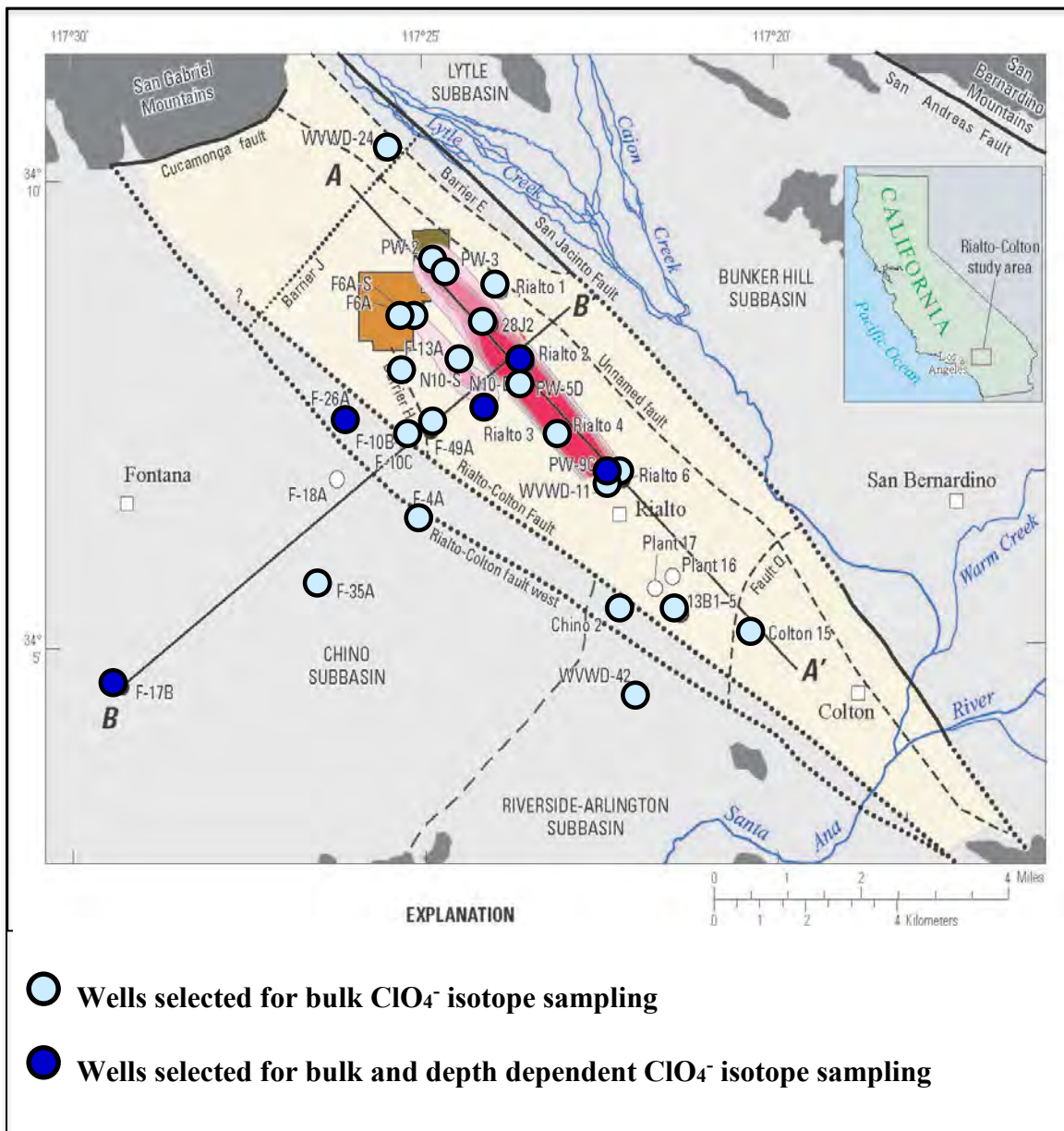
**Figure 1.3.** Values of  $^{36}\text{Cl}/\text{Cl}$  (mole fraction) versus  $\delta^{37}\text{Cl}$  (‰) in representative samples of synthetic  $\text{ClO}_4^-$  reagents and products, natural  $\text{ClO}_4^-$  extracted from soil and groundwater from the Atacama Desert, Chile, and natural  $\text{ClO}_4^-$  extracted from groundwater and soil from the southwestern U.S. (modified from Sturchio et al., 2009).

## **2.0 Materials and Methods**

### **2.1 Selection of Wells for Groundwater Sample Collection**

In the early phase of this project, U.S. Geological Survey (USGS) personnel in San Diego, CA compiled a GIS database of groundwater wells in the Study Area using information from numerous sources, including the California Department of Public Health, USGS National Water Information System, U.S. Environmental Protection Agency (EPA), County of San Bernardino, and various local water agencies and consultants. From this database, a preliminary group of 27 groundwater wells in the Rialto-Colton and Chino subbasins was selected by the project team for isotopic sampling, and 16 wells were selected as possible alternates. North-south and east-west transects across the two synthetic plumes were used as a basis for well selection. These transects included wells within each of the two defined plume areas, and wells that were upgradient (northwest), downgradient (southeast), and crossgradient (northeast and southwest) of the mapped plume areas. Wells were also selected on each side of, and in close proximity to, the Rialto-Colton Fault, and between the Rialto-Colton Fault and the Rialto-Colton Fault-West. Wells selected for sample collection were reviewed by a Technical Advisory Committee (TAC) established for the project which included local water purveyors, regulatory agencies, and other stakeholders. Substitutions of wells were made at the suggestion of the TAC and in the field, where necessary to meet the objectives of this study, when initial well selections were precluded based on well conditions and/or well accessibility, low  $\text{ClO}_4^-$  concentrations, or other issues observed in the field.

A total of 27 wells (17 production wells, 8 monitoring wells, and 2 Westbay wells) were selected and sampled for  $\text{ClO}_4^-$  isotopes (Figure 2.1). In addition, in conjunction with coupled well bore-flow and depth-dependent water quality sampling (Izbicki et al., 2014), depth-dependent  $\text{ClO}_4^-$  stable isotope samples were collected from five of the production wells (Rialto 2, Rialto 3, Rialto 6, F-17B, F-26A). Additional details on the study area hydrogeology and well characteristics are provided in a previously published paper (Izbicki et al., 2014).



**Figure 2.1. Wells selected for bulk discharge  $\text{ClO}_4^-$  isotope sampling (light blue symbols) and depth-dependent  $\text{ClO}_4^-$  isotope sampling (dark blue symbols).** Depth-dependent well bore flow and water quality analysis was also performed on wells F-10C and F-49A (see Izbicki et al., 2014). The map does not include concentration data from this study, the most recent USEPA site sampling (USEPA, 2014) or Izbicki et al. (2014). See Figure 1.1 for explanation of map.



## 2.2 Groundwater Sampling Procedure

Approximately 20  $\mu\text{mol}$  of pure  $\text{ClO}_4^-$  salt (as  $\text{KClO}_4$ , prepared as described in Section 2.3) is normally sufficient to obtain duplicate stable isotope ratio measurements by IRMS for both O and Cl in the  $\text{ClO}_4^-$  ion, as well as a measurement of  $^{36}\text{Cl}$  isotopic abundance. However, because of potential losses during sample collection and purification (Section 2.3), and allowing sufficient sample for additional replicate analyses, it is generally desirable to collect samples containing at least 100  $\mu\text{mol}$  (i.e. 10 mg) of  $\text{ClO}_4^-$  from each source. For groundwaters having low  $\text{ClO}_4^-$  concentrations (i.e.,  $< 5 \mu\text{g/L}$ ), shipping enough water to obtain 10 mg of  $\text{ClO}_4^-$  is impractical. Instead, small columns containing about 100 mL ( $\sim 60$  g dry wt) of Purolite A-530E  $\text{ClO}_4^-$ -specific anion exchange resin (IX resin) have been developed to preconcentrate  $\text{ClO}_4^-$  from large volumes of water in the field. Water is passed through these columns, and the  $\text{ClO}_4^-$  is trapped by the IX resin. Although many hours may be required for sample collection in some cases, the columns are capable of trapping 10 mg of  $\text{ClO}_4^-$  on a small volume of resin. The  $\text{ClO}_4^-$  is then extracted from the resin and purified prior to IRMS analyses, as described in Section 2.3.

For this project, the USGS performed all groundwater sampling, as described elsewhere (Izbicki et al., 2014). Resin columns were used for sample collection from all wells, except the Westbay wells for which aqueous  $\text{ClO}_4^-$  concentrations were high enough for water to be collected and shipped directly to the laboratory without using the IX column collection technique. All IX columns for sampling were prepared at the Environmental Isotope Geochemistry Laboratory (EIGL) of the University of Illinois at Chicago (UIC) and sent directly to the USGS with unique identification numbers. In many instances, two or more (up to 8) columns were set up at a single well to collect enough  $\text{ClO}_4^-$  for stable isotope analysis from low-concentration waters, and in some cases to provide independent replicate samples for isotopic analysis so that method reproducibility could be evaluated. In some cases, groundwater was passed through columns for as long as two weeks to accumulate sufficient  $\text{ClO}_4^-$  for analysis. The original goal of this project was to conduct duplicate analyses (i.e, process and analyze independent sample columns) on 25% of the wells sampled. This goal was exceeded, as

replicate samples were obtained for 10 of the 33 well locations (wells plus depth-dependent samples).

Most production wells were sampled from the surface discharge of the existing well pump. Depth-dependent samples were collected from selected depths within five production wells under pumping conditions (see Izbicki et al., 2014). Sample depths were identified on the basis of available geologic and geophysical logs and unpumped and pumped well-bore flow logs collected as part of the study. Samples from those wells also were collected from the surface discharge of a temporary pump installed within the well after the production pump was removed. Monitoring wells were sampled using a positive displacement gas-reciprocating pump (Bennett pump) capable of lifting water from depths greater than 200 m below land surface (bls). Production and monitoring wells were purged to remove at least three casing volumes prior to sample collection. Field parameters (pH, temperature, and specific conductance) were monitored during purging using a thermometer and portable meters. After field parameters stabilized, groundwater samples were collected for measurement of major ion concentrations (including  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ ), groundwater dating parameters, dissolved gases, and  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in water, as described in Izbicki et al. (2014). Samples were collected from Westbay installations using equipment designed by the manufacturer for this purpose.

At the conclusion of all required water quality sampling, one (or more) ion exchange column(s) was connected to the groundwater discharge from each well pump. The flow to the columns was generally set at 1 to 2.5 liters per minute (LPM). Periodically, samples were collected from the influent and effluent of the columns to evaluate stability of influent concentration with time, to detect column breakthrough of  $\text{ClO}_4^-$ , and to estimate the total amount of  $\text{ClO}_4^-$  trapped on each column. After a pre-determined time, ranging from a few hours to as long as two weeks (based on flow rate and starting  $\text{ClO}_4^-$  concentration in each well), the IX columns were removed from the each well, sealed in Zip-Loc type bags, placed at 4°C (or on ice), and shipped to the UIC EIGL for  $\text{ClO}_4^-$  extraction and purification.

## 2.3 Sample Purification and Isotopic Analysis

### 2.3.1 Sample purification

The preparation of  $\text{ClO}_4^-$  present on the IX resin for chlorine and oxygen isotope ratio analysis involved two main procedures prior to IRMS: (1) elution and recovery of  $\text{ClO}_4^-$  from the resin and (2) separation of  $\text{ClO}_4^-$  from other materials trapped on the IX resin, including a variety of anions and organics. The sample elution and purification procedures were conducted by laboratory technicians under the supervision of Dr. Neil Sturchio at UIC EIGL. Briefly, the key steps in the extraction and purification method were as follows: (1) the resin was washed ultrasonically with deionized water (DIW) and flushed with several pore volumes of 4M HCl to remove adsorbed  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , and some of the humics, but not  $\text{ClO}_4^-$  which is more strongly held by the bifunctional resin than most other anions or organics; (2)  $\text{ClO}_4^-$  was eluted from the resin bed using 1 M  $\text{FeCl}_3$ -4M HCl solution (Gu et al., 2001, 2011); (3) eluted  $\text{ClO}_4^-$  was purified by a series of cation exchange, oxidation, and evaporation steps; (4) KOH was added to precipitate  $\text{KClO}_4$  for isotopic analysis; and (5)  $\text{KClO}_4$  crystals were washed with methanol and their purity was measured by ion chromatography (IC).

Tetrachloroferrate ( $\text{FeCl}_4^-$ ) ions are present in the 1 M  $\text{FeCl}_3$  and 4 M HCl eluant solution and these ions remove  $\text{ClO}_4^-$  from the Purolite A530E resin (Gu et al., 2001). The  $\text{FeCl}_3$ -HCl eluent containing dissolved  $\text{ClO}_4^-$  was diluted to convert  $\text{FeCl}_4^-$  to cationic  $\text{Fe}^{3+}$  species, then it was passed through a large glass chromatography column packed with AG-50W-X12 resin to remove Fe. The eluent from this column was collected and evaporated on a hot plate, with addition of several mL concentrated  $\text{H}_2\text{O}_2$  to oxidize organic compounds, until the remaining solution volume was reduced to about 50 mL. The evaporation produces an azeotropic mixture (~6 M HCl) so that most of the excess HCl was removed by evaporation. To separate residual  $\text{NO}_3^-$  from  $\text{ClO}_4^-$ , the concentrated sample was reloaded onto 1 mL of A530E resin, flushed with 4 M HCl, re-eluted with  $\text{FeCl}_3$ -HCl, and the resulting eluent evaporated to <5 mL. The remaining excess dissolved  $\text{Cl}^-$  (HCl) was then removed by passing the sample through an OnGuard II Ag Sample Pretreatment Cartridge (Dionex, Sunnyvale, California). OnGuard II H (cation-exchange hydronium form resin) cartridges were then used to remove any dissolved Ag. Residual organics were removed by oxidation with  $\text{H}_2\text{O}_2$  or by Strata

SDB-L (Phenomenex, Torrance, California) solid phase extractant.

The  $\text{ClO}_4^-$  in solution was then precipitated with an excess of KOH to produce  $\text{KClO}_4$ . Residual KOH was removed from  $\text{KClO}_4$  by rinsing the residue with methanol. The  $\text{KClO}_4$  crystals were then collected by filtration and rinsed with a few drops of 90 % methanol (by volume, in water). The purified  $\text{KClO}_4$  was then dissolved in DIW and a small aliquot was analyzed by IC to assess purity, with a target of <1% anionic impurities. If necessary to achieve target purity, samples were further treated by addition of tetrapentylammonium bromide (TPABr) to precipitate  $\text{ClO}_4^-$  as  $\text{TPAClO}_4$ , followed by ethanol washing to remove excess TPABr, followed by reaction of  $\text{TPAClO}_4$  with KOH-methanol solution to reprecipitate  $\text{KClO}_4$  (Poghosyan et al., 2014). The final  $\text{KClO}_4$  product was rinsed with ethanol and redissolved in DIW for IC analysis of purity. Mass balance of O during sample decomposition for O isotope analysis was evaluated subsequently to further assess sample purity (i.e., to determine if the sample yielded more or less O than expected from pure  $\text{KClO}_4$ ). In some samples, presence of C or N was also evaluated as part of the IRMS analysis (See Section 2.3.2).

### 2.3.2 Analysis of Oxygen Isotope Ratios in Perchlorate by IRMS

After the  $\text{KClO}_4$  was purified according to the procedures described in the previous section, it was analyzed for O and Cl isotopic composition by IRMS according to the procedures described in this section for O and in Section 2.3.3 for Cl. Analysis of O isotopes in  $\text{ClO}_4^-$  was conducted by three different methods when sufficient sample was available. These methods were (1) Off-line conversion to  $\text{O}_2$  with dual-inlet isotope-ratio mass spectrometry using a liquid nitrogen trap ( $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$ ); (2) Off-line conversion to  $\text{O}_2$  with dual-inlet isotope-ratio mass spectrometry without a liquid nitrogen trap ( $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$ ); and (3) On-line conversion to CO, with continuous-flow isotope-ratio mass spectrometry (CO-CF-IRMS). The  $\text{O}_2\text{-DI-IRMS}$  method yielded values of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\Delta^{17}\text{O}$  in  $\text{O}_2$  gas. A liquid  $\text{N}_2$  trap ( $+\text{N}_2$ ) minimized potential interferences caused by condensable gases (e.g.,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) entering the IRMS with the  $\text{O}_2$  sample; thus  $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$  was the primary method applied to all samples. Performed without a liquid  $\text{N}_2$  trap ( $-\text{N}_2$ ), this method permitted condensable gases to enter the IRMS where they could be ionized and measured. The  $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$

method was used to evaluate contaminants and co-products of  $\text{ClO}_4^-$  decomposition. The CO-CF-IRMS method yielded values of  $\delta^{18}\text{O}$ , but not  $\delta^{17}\text{O}$  or  $\Delta^{17}\text{O}$ . This method included measurement of the relative amount of  $\text{N}_2$  as an indication of potential contamination by air or N-O salts such as  $\text{NO}_3^-$  and it was used selectively as an independent test for major problems with the  $\text{O}_2$  methods. The methods are described in more detail in sections 2.3.2.1 and 2.3.2.2.

All samples were analyzed at least once by  $\text{O}_2$ -DI-IRMS(+ $\text{N}_2$ ), and many samples were analyzed multiple times. The data from this technique were used for comparisons provided in the *Results and Discussion* section, and generally for the stable isotope data published previously by this group (e.g., Böhlke et al., 2009; Jackson et al., 2010). Most samples were also analyzed by  $\text{O}_2$ -DI-IRMS(- $\text{N}_2$ ) to determine approximate relative susceptibility of O isotopes to C contamination effects. Relatively few samples were analyzed by CO-CFIRMS, as this method was not compatible with Cl isotopic analysis. Data from all three techniques are summarized in Section 3.4 (Table 3.7; Figure 3.10).

#### 2.3.2.1 Analysis of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ by Off-Line Conversion to $\text{O}_2$ , with Dual-Inlet IRMS ( $\text{O}_2$ -DI-IRMS)

To perform DI-IRMS on  $\text{O}_2$  derived from  $\text{ClO}_4^-$ , aliquots of pure  $\text{KClO}_4$  were weighed into quartz glass tubes (mass equivalent to 2.5  $\mu\text{mol}$  of  $\text{ClO}_4^-$  per tube). The tubes were evacuated and sealed with a torch and then baked at 650  $^\circ\text{C}$  for 20 min to produce  $\text{O}_2$  gas from the  $\text{ClO}_4^-$ . The tubes were broken manually in an evacuated tube cracker, and the  $\text{O}_2$  expanded into a liquid  $\text{N}_2$  cold trap for 1 min to remove traces of condensable gases ( $\text{O}_2$ -DI-IRMS (+ $\text{N}_2$ )) or no  $\text{N}_2$  trap was used ( $\text{O}_2$ -DI-IRMS (- $\text{N}_2$ )) if the effects of condensable gases were under study. The  $\text{O}_2$  was then admitted to an IRMS and analyzed in dual-inlet mode against an  $\text{O}_2$  reference gas from a tank by monitoring  $m/z$  32 ( $^{16}\text{O}^{16}\text{O}$ ), 33 ( $^{17}\text{O}^{16}\text{O}$ ), and 34 ( $^{18}\text{O}^{16}\text{O}$ , plus an insignificant contribution from  $^{17}\text{O}^{17}\text{O}$ ). Typical reproducibility of  $\delta^{18}\text{O}$  measurements by  $\text{O}_2$ -DI-IRMS on multiple aliquots of  $\text{KClO}_4$  (typically three to four) in a given batch is generally around  $\pm 0.2\text{‰}$  or better for the reference material USGS37 and  $\pm 0.5\text{‰}$  or better for the reference material USGS38 (Hatzinger et al., 2011).

#### *2.3.2.2 Analysis of $\delta^{18}\text{O}$ by On-Line Conversion to CO, with Continuous-Flow IRMS (CO-CF-IRMS)*

To perform CF-IRMS on CO derived from  $\text{ClO}_4^-$ , aliquots of pure  $\text{KClO}_4$  were weighed into silver foil cups (mass equivalent to 2  $\mu\text{mol}$  of  $\text{ClO}_4^-$  per cup). The loaded cups were dropped automatically from a He-flushed carousel into a graphite crucible in a glassy carbon reactor at a nominal (gauge) temperature of 1325°C to produce CO gas from the  $\text{ClO}_4^-$ . The CO was transferred in He carrier gas through a molecular-sieve gas chromatograph to an IRMS and analyzed in continuous-flow mode by monitoring peaks at  $m/z$  28 ( $^{12}\text{C}^{16}\text{O}$ ) and 30 ( $^{12}\text{C}^{18}\text{O}$ , plus an insignificant contribution from  $^{13}\text{C}^{17}\text{O}$ ). Typical reproducibility of  $\delta^{18}\text{O}$  measurements by CO-CF-IRMS on multiple aliquots (typically four to eight) in a given batch is generally around  $\pm 0.2\text{‰}$  or better for USGS37 and  $\pm 0.2\text{‰}$  or better for USGS38 (Hatzinger et al., 2011).

#### 2.3.3 Analysis of Chlorine Isotope Ratios in Perchlorate by IRMS

The analysis of Cl stable isotope ratios was conducted on the KCl produced by thermal decomposition of  $\text{KClO}_4$  as described in Section 2.3.2.2 for production of  $\text{O}_2$ . The  $\text{Cl}^-$  derived from  $\text{ClO}_4^-$  was converted to methyl chloride ( $\text{CH}_3\text{Cl}$ ) gas (Eggenkamp, 1994; Holt et al., 1997), which was then analyzed by IRMS according to the procedures described in this section. The methods and calibrations of Cl isotopic analyses from  $\text{ClO}_4^-$  have been summarized in several papers and book chapters as described previously, and additional details on method procedures and QA/QC are given in Hatzinger et al. (2011).

##### *2.3.3.1 Analysis of $\delta^{37}\text{Cl}$ by Off-Line Conversion to Methyl Chloride, with Dual-Inlet IRMS ( $\text{CH}_3\text{Cl}$ -DI-IRMS)*

Chlorine isotopic analyses were performed on samples of KCl from decomposition of  $\text{ClO}_4^-$  salts as described above for preparation of  $\text{O}_2$  for isotopic analysis (Section 2.3.2). KCl residue in a decomposition tube was dissolved using 10 mL of warm 18.2 M $\Omega$  deionized water. The dissolved alkali halide residue was transferred into a 50-mL polypropylene conical tube and acidified with 100  $\mu\text{L}$  concentrated nitric acid ( $\text{HNO}_3$ ). This solution was then heated to 80 °C and an excess of silver nitrate

(AgNO<sub>3</sub>) was added as described in Eggenkamp (1994). Silver chloride (AgCl) precipitates were then allowed to ripen in a dark cabinet for ~ 24 hr. The AgCl solids were then centrifuged, the supernatant was removed, and 0.03 M HNO<sub>3</sub> was used to rinse the solids three times. Solids were then transferred into a Pyrex combustion tube (20 cm x 9 mm) and dried in a darkened vacuum oven at 80 °C. After the sample was dry, the combustion tube was evacuated and CH<sub>3</sub>I was cryogenically transferred into the tube which was then sealed and baked for 2 h at 300 °C as described in Holt et al. (1997). The resulting CH<sub>3</sub>Cl was purified using gas chromatography, cryo-concentrated, and then admitted to the IRMS and analyzed in dual-inlet mode by monitoring peaks at *m/z* 52 (<sup>12</sup>C<sup>1</sup>H<sub>3</sub><sup>37</sup>Cl) and 50 (<sup>12</sup>C<sup>1</sup>H<sub>3</sub><sup>35</sup>Cl). Typical reproducibility of δ<sup>37</sup>Cl measurements on multiple aliquots in a given batch are generally ±0.2‰ or better for USGS37 and ±0.3‰ or better for USGS38 (Hatzinger et al., 2011).

#### 2.3.4 Standards for Oxygen and Chlorine Stable Isotopic Analysis

Equations 1.1 and 1.2 are expanded to permit routine calibration of ClO<sub>4</sub><sup>-</sup> analyses using a pair of ClO<sub>4</sub><sup>-</sup> isotopic reference materials (USGS37 and USGS38) (see description in Hatzinger et al., 2011) with contrasting isotopic compositions on the VSMOW-SLAP scale, a process commonly referred to as “normalization”:

$$\begin{aligned} \text{[Eq. 2.1]} \quad \delta^{18}\text{O}_{\text{i/VSMOW}} &= \delta^{18}\text{O}_{37/\text{VSMOW}} + \\ &[\delta^{18}\text{O}_{\text{i/rg}} - \delta^{18}\text{O}_{37/\text{rg}}]_{\text{meas.}} \cdot [\delta^{18}\text{O}_{38/\text{VSMOW}} - \delta^{18}\text{O}_{37/\text{VSMOW}}] / [\delta^{18}\text{O}_{38/\text{rg}} - \delta^{18}\text{O}_{37/\text{rg}}]_{\text{meas.}} \end{aligned}$$

$$\begin{aligned} \text{[Eq. 2.2]} \quad \delta^{17}\text{O}_{\text{i/VSMOW}} &= \delta^{17}\text{O}_{37/\text{VSMOW}} + \\ &[\delta^{17}\text{O}_{\text{i/rg}} - \delta^{17}\text{O}_{37/\text{rg}}]_{\text{meas.}} \cdot [\delta^{17}\text{O}_{38/\text{VSMOW}} - \delta^{17}\text{O}_{37/\text{VSMOW}}] / [\delta^{17}\text{O}_{38/\text{rg}} - \delta^{17}\text{O}_{37/\text{rg}}]_{\text{meas.}}, \end{aligned}$$

where 37 and 38 refer to the ClO<sub>4</sub><sup>-</sup> isotopic reference materials USGS37 and USGS38, and rg is an internal laboratory reference gas (either CO or O<sub>2</sub>) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses.

The isotopic reference materials consist of reagent-grade KClO<sub>4</sub> salts that were prepared specifically for calibration of ClO<sub>4</sub><sup>-</sup> isotopic analyses. The δ<sup>18</sup>O scale is based

on CO-CF-IRMS analyses of the  $\text{ClO}_4^-$  isotopic reference materials against international  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  isotopic reference materials as described by Böhlke et al. (2003), and all data are referenced to the conventional VSMOW-SLAP scale (Gonfiantini, 1978; Coplen, 1994). For  $\delta^{18}\text{O}$ , the secondary calibration values used to generate provisional  $\text{ClO}_4^-$  data with respect to VSMOW are -27.9 ‰ for USGS34 ( $\text{KNO}_3$ ), +25.6 ‰ for IAEA-N3 ( $\text{KNO}_3$ ), +57.5 ‰ for USGS35 ( $\text{NaNO}_3$ ), and +8.6 ‰ for NBS 127 ( $\text{BaSO}_4$ ) (Böhlke et al., 2003). The  $\delta^{17}\text{O}$  scale for  $\text{ClO}_4^-$  is provisionally based on the assumption that the normal reagent  $\text{KClO}_4$  reference material (USGS37) has  $R(^{17}\text{O}/^{16}\text{O})$  and  $R(^{18}\text{O}/^{16}\text{O})$  values that are related to those of VSMOW by mass-dependent processes ( $\Delta^{17}\text{O} = 0$  as defined by Equation 1.4; Böhlke et al., 2005). Perchlorate calibration values used for data normalization in this study are consistent with those reported previously (Böhlke et al., 2009): for USGS37,  $\delta^{18}\text{O} = -17.00$  ‰ and  $\delta^{17}\text{O} = -8.96$  ‰; for USGS38,  $\delta^{18}\text{O} = +52.5$  ‰ and  $\delta^{17}\text{O} = +102.5$  ‰. For USGS37, our  $\Delta^{17}\text{O}$  value of 0.0 ‰ defined by Equation 1.4 is in agreement with a mean value of  $-0.11 \pm 0.06$  ‰ reported for synthetic  $\text{ClO}_4^-$  using an alternative  $\Delta^{17}\text{O}$  definition (Bao and Gu, 2004).

The most widely-used Cl isotope reference material is chloride prepared from seawater which has uniform  $\delta^{37}\text{Cl}$  to within  $\pm 0.08$  ‰ (Godon et al., 2004). Routine calibration of  $\text{ClO}_4^-$  isotopic analyses was also conducted by using the pair of  $\text{ClO}_4^-$  isotopic reference materials (USGS37 and USGS38) as follows:

$$[\text{Eq. 2.3}] \quad \delta^{37}\text{Cl}_{i/\text{SMOC}} = \delta^{37}\text{Cl}_{37/\text{SMOC}} + [\delta^{37}\text{Cl}_{i/\text{rg}} - \delta^{37}\text{Cl}_{37/\text{rg}}]_{\text{meas.}} \cdot [\delta^{37}\text{Cl}_{38/\text{SMOC}} - \delta^{37}\text{Cl}_{37/\text{SMOC}}] / [\delta^{37}\text{Cl}_{38/\text{rg}} - \delta^{37}\text{Cl}_{37/\text{rg}}]_{\text{meas.}}$$

where, as with O isotope analysis, 37 and 38 refer to the perchlorate isotopic reference materials USGS37 and USGS38, and rg is an internal laboratory reference gas ( $\text{CH}_3\text{Cl}$ ) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses. Perchlorate calibration values used in this study are (Böhlke et al., 2009): for USGS37,  $\delta^{37}\text{Cl} = +0.6$  ‰; for USGS38,  $\delta^{37}\text{Cl} = -87.2$  ‰.



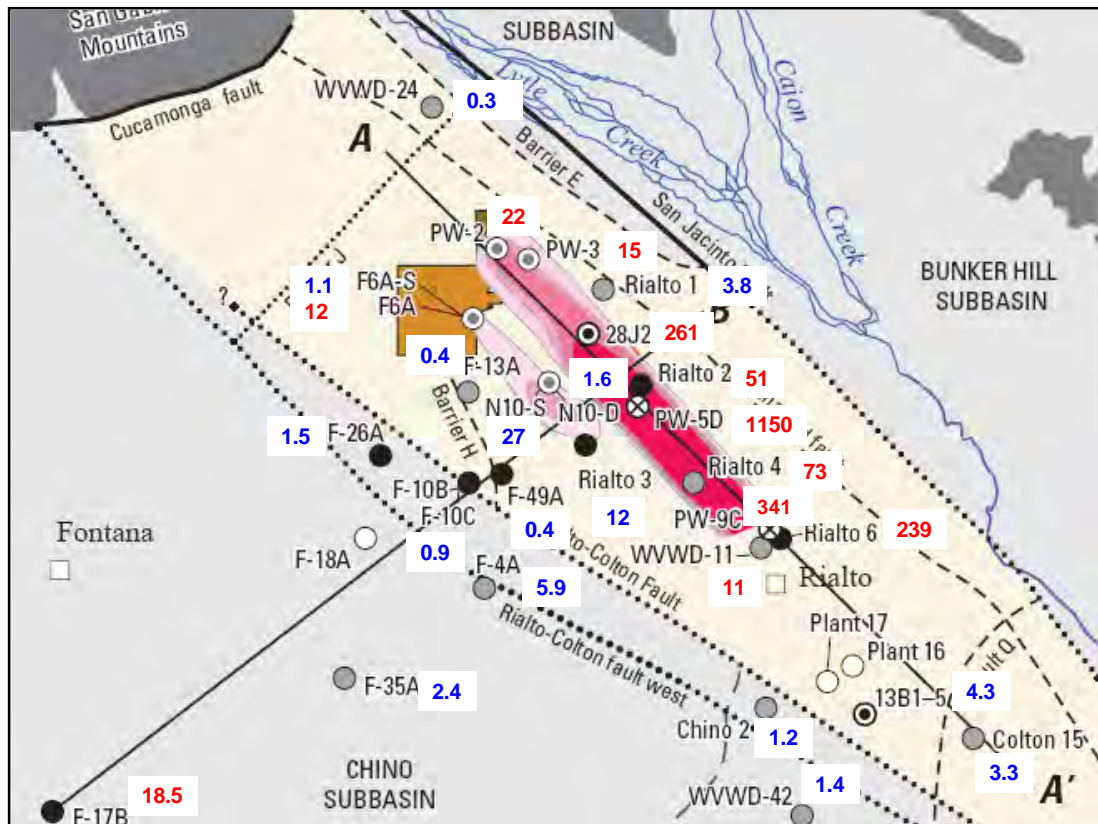
#### 2.3.5 Analysis of $^{36}\text{Cl}$ in $\text{ClO}_4^-$

Analysis of  $^{36}\text{Cl}$  in  $\text{ClO}_4^-$  was performed by accelerator mass spectrometry (AMS) using  $\text{Cl}^-$  derived from  $\text{ClO}_4^-$ . The  $^{36}\text{Cl}$  analyses on  $\text{ClO}_4^-$  collected during this project were performed at the Purdue Rare Isotope Measurement Laboratory (PRIME) at Purdue University ([www.physics.purdue.edu/primelab](http://www.physics.purdue.edu/primelab)). The procedure used to produce  $\text{Cl}^-$  for AMS is as described in Section 2.3.3 of this document to the point of  $\text{AgCl}$  precipitation, washing, and drying of crystals (i.e., prior to the reaction with  $\text{CH}_3\text{I}$ ). A portion of the sample prepared to this step for  $\text{Cl}$  stable isotopic analysis was saved for  $^{36}\text{Cl}$  analysis. The  $\text{AgCl}$  was subsequently re-dissolved and the  $\text{Cl}^-$  purified twice by anion chromatography (using a method developed by the PRIME Lab at Purdue University; <http://www.physics.purdue.edu/primelab/AMSQAQC/chemProc004.pdf>) to ensure removal of trace amounts of S that might cause isobaric interference at mass 36. Purified  $\text{Cl}^-$  is then re-precipitated as  $\text{AgCl}$  for AMS measurement. Analysis of seawater  $\text{Cl}^-$  provides a reference datum of  $^{36}\text{Cl}/\text{Cl}$  with a value of  $0.5 \times 10^{-15}$  (Argento et al., 2010).

### 3.0 Results and Discussion

#### 3.1 ClO<sub>4</sub><sup>-</sup> Concentrations in Groundwater Wells

Measured concentrations of ClO<sub>4</sub><sup>-</sup> in Study Area groundwater ranged from 0.3 µg/L to 1,150 µg/L in wells that were sampled for ClO<sub>4</sub><sup>-</sup> isotopes (Figure 3.1; Table 3.1). With the exception of Well F-17B in the Chino subbasin, all of the wells with concentrations above the California MCL of 6 µg/L were located within the two mapped ClO<sub>4</sub><sup>-</sup> plumes (Figure 3.1). In general, the average influent concentrations from the IX columns used to collect ClO<sub>4</sub><sup>-</sup> for isotopic analysis were similar to the individual samples taken for ClO<sub>4</sub><sup>-</sup> analysis (Table 3.1). A statistical analysis of the variation of ClO<sub>4</sub><sup>-</sup> concentration entering the columns with time is provided in Izbicki et al., (2014). There was no apparent correlation between the average ClO<sub>4</sub><sup>-</sup> concentration and the variability in that concentration.



**Figure 3.1. Concentration of ClO<sub>4</sub><sup>-</sup> in groundwater wells during stable isotope sampling.** Values provided are the average influent concentration to IX columns used for groundwater sampling except for F-10C, F-49A, PW-5D and PW-9C, where individual analyses are provided. Concentrations above 6 µg/L are shown in red, and those below 6 µg/L are shown in blue. See Figure 1.1 for explanation of the map.

### 3.2 Isotope Results for $\text{ClO}_4^-$

The Cl and O stable isotope results for  $\text{ClO}_4^-$  in Study Area well samples are provided in dual isotope plots in comparison to previous source data for synthetic, Atacama, and selected indigenous natural  $\text{ClO}_4^-$  samples (SHP, MRGB, and Death Valley caliche) in Figures 3.2 and 3.3. The isotopic values ( $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{Cl}$ , and  $^{36}\text{Cl}/\text{Cl}$ ) are plotted with respect to the inverse of the measured  $\text{ClO}_4^-$  concentrations in Figure 3.4 to illustrate potential mixing and dilution trends. Average isotope values and  $\text{ClO}_4^-$  concentrations in the column influent are provided in Table 3.1.

In general, it appears that  $\text{ClO}_4^-$  from all three proposed sources was present in varying proportions in Study Area groundwater (Figures 3.2-3.4). Samples having relatively high  $\text{ClO}_4^-$  concentrations (values of inverse  $\text{ClO}_4^-$  concentration  $< 1$ , i.e.  $\text{ClO}_4^-$  concentrations  $> 1 \mu\text{g/L}$ ) generally plot near a single dominant  $\text{ClO}_4^-$  source, either synthetic or Atacama (Figure 3.4), whereas samples having lower concentrations commonly indicate mixtures with varying fractions of indigenous natural  $\text{ClO}_4^-$ . These relations are consistent with the presence of a low background concentration of indigenous  $\text{ClO}_4^-$ , toward which the isotopic composition of  $\text{ClO}_4^-$  converges as fractions of the other two  $\text{ClO}_4^-$  sources approach zero (Figure 3.4).

To facilitate discussion of results, hypothetical mixing zones among three potential  $\text{ClO}_4^-$  endmembers (synthetic, Atacama, indigenous) are plotted with the Study Area stable isotope data ( $\delta^{37}\text{Cl}$  vs  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{Cl}$  vs  $\delta^{18}\text{O}$ ) and with  $^{36}\text{Cl}$  data ( $^{36}\text{Cl}/\text{Cl}$  vs  $\delta^{37}\text{Cl}$ ) in Figure 3.5. A similar three-endmember mixing approach was also recently used to determine the dominant source of  $\text{ClO}_4^-$  in groundwater of the nearby location of Pomona, CA, using  $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  data ( $^{36}\text{Cl}$  values were not reported) (Sturchio et al., 2014). Characteristics of three  $\text{ClO}_4^-$  endmembers for the Study Area groundwaters were determined as follows: (1) The Atacama and synthetic endmembers were obtained by separate linear least-squares regressions of  $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ , and  $\Delta^{17}\text{O}$  values vs. inverse  $\text{ClO}_4^-$  concentrations. This procedure is based on the assumption that all samples may have varying amounts of background  $\text{ClO}_4^-$ , and the Atacama and synthetic endmembers are most likely to dominate at high concentrations (Sturchio et al., 2014). The best-fit regression parameters (slope and intercept, with 2-sigma errors) for samples having  $\text{ClO}_4^-$  concentrations exceeding  $1 \mu\text{g/L}$  were determined using the regression function of Microsoft Excel. This concentration cutoff was based on the fact that samples in this

concentration range could clearly be seen as having either a dominantly Atacama or dominantly synthetic source, based on all three stable isotope values (see Figure 3.4). (2) For the indigenous endmember, no sample of  $\text{ClO}_4^-$  was obtained from the Study Area that was clearly of “pure” indigenous origin, so published data for the SHP and MRGB groundwater  $\text{ClO}_4^-$  samples from Sturchio et al. (2006) and Jackson et al. (2010) were used to define its stable isotopic composition (Sturchio et al., 2014). This represents one possible endmember choice, and other alternatives are also discussed below. (3) Because of relatively large variability in measured  $^{36}\text{Cl}/\text{Cl}$  ratios (particularly for samples relatively enriched in the indigenous endmember), in contrast with the stable isotope ratios, regression analysis did not yield precise estimates of  $^{36}\text{Cl}/\text{Cl}$  ratios in the dominant endmembers from the Study Area. Therefore, medians and ranges of published values were used to represent  $^{36}\text{Cl}/\text{Cl}$  ratios of all three endmembers in mixing calculations (Sturchio et al., 2009; Jackson et al., 2010; Poghosyan et al., 2014). The endmember values used for the analysis are provided in Table 3.2 (mean and 2-sigma errors).

The  $\delta^{37}\text{Cl}$  vs.  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ , and  $^{36}\text{Cl}/\text{Cl}$  vs.  $\delta^{37}\text{Cl}$  plots of Study Area sample data, in comparison with the three  $\text{ClO}_4^-$  source endmembers defined above, indicate that the proposed three-component mixing is capable of accounting for the observed variations in isotopic composition in nearly all samples, given uncertainties and potential variability of endmember characteristics (Figure 3.5). The mixing regions between the end members (shown as boxes with each side being the limit of 2-sigma error) are indicated by the gray lines in Figure 3.5. The mixing results in Figure 3.5, as well as the  $\Delta^{17}\text{O}$  vs  $1/\text{concentration}$  plot in Figure 3.4, indicate that the  $\Delta^{17}\text{O}$  range of the proposed indigenous Study Area endmember is similar to that in the SHP, MRGB, eastern Oregon and Great Lakes samples (i.e., +0.3 to +2.9 ‰) rather than the much higher range observed for Death Valley caliche samples (i.e., + 8.6 to +18.4 ‰) (Jackson et al., 2010; Hatzinger et al., 2013; Poghosyan et al., 2014).

To estimate mixing fractions of each of the three endmembers in the Study Area samples, the average values of all stable isotope ratio analyses for each well (from Table 3.1) along with endmember mean values and standard deviations (from Table 3.2) were used as input for the spreadsheet program *IsoError1\_04.xls* [described in Phillips and Gregg (2001) and in the instructions accompanying the spreadsheet]. These spreadsheet calculations yielded quantitative endmember fractions for each sample, based on

assumptions given above, accounting for sample measurement uncertainties and population sizes of endmembers. Mixing fractions were calculated with 2-sigma error estimates from three pairs of isotope values,  $\delta^{37}\text{Cl}$  vs.  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ , and  $^{36}\text{Cl}/\text{Cl}$  vs.  $\delta^{37}\text{Cl}$ . The 95 % confidence limits (maximum and minimum mixing fractions) from these calculations are provided in Table 3.3 to Table 3.5. Mixing fractions calculated from  $\delta^{37}\text{Cl}$  vs.  $\delta^{18}\text{O}$  generally agree with those calculated from  $\Delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ ; there is a cluster of samples near the Atacama endmember, a cluster of samples near the synthetic endmember, and a few intermediate mixed samples (that are also the samples with the lowest total  $\text{ClO}_4^-$  concentrations). Some calculated maximum values of mixing fractions at a 95 % confidence interval exceeded 1 (with a maximum value of 1.1) and a few of the minimum values were negative at a 95 % confidence limit (with a minimum value of -0.2), reflecting uncertainties in the assumed endmember characteristics. The dominant sources indicated by the  $^{36}\text{Cl}/\text{Cl}$  vs  $\delta^{37}\text{Cl}$  mixing analysis were generally consistent with those determined using the stable isotope values (Table 3.5). The data also indicated minor fractions of indigenous  $\text{ClO}_4^-$  in many of the samples as is apparent in Figure 3.5 and discussed in more detail later in this section.

Measured values of  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  were consistent with those of synthetic  $\text{ClO}_4^-$  sources for all sampled wells located in the perched aquifer within the two mapped  $\text{ClO}_4^-$  plumes (28J-2, F-6, F6A-S, N-10S) (Figures 3.3-3.5; Tables 3.1, 3.3, 3.4). Similarly, isotopic data from wells in the regional aquifer within the mapped plumes also were consistent with a dominantly synthetic source (with minimum mixing fractions generally ranging from 60 – 90% and maximum fractions at 100 to 110 % using a 95 % confidence interval), including PW-2, PW-3, Rialto 2, Rialto 2 (880'), PW-5D, Rialto 3, Rialto 3 (670'), PW-9C, Rialto 6, Rialto 6 (480'), Rialto 6 (560'), and Rialto 4) (Table 3.3, 3.4). All of these samples had mean  $\delta^{37}\text{Cl}$  values between -1.0 and +1.5 ‰ and  $\Delta^{17}\text{O}$  values between -0.1 and +0.2 ‰, consistent with dominantly synthetic  $\text{ClO}_4^-$ . The  $\delta^{18}\text{O}$  values varied from -12.5 to -20.3 ‰, also within the range previously reported for synthetic  $\text{ClO}_4^-$  sources. However, the relatively wide range in  $\delta^{18}\text{O}$  for these samples also appears to reflect mixing with small fractions of natural indigenous  $\text{ClO}_4^-$  (see next paragraph) in addition to possible variation in synthetic source isotopic ratios.

**Table 3.1. Perchlorate concentrations and Cl and O isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.**

State well number	Local well name	Date	$\delta^{37}\text{Cl}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$^{36}\text{Cl}$ $^{36}\text{Cl}/\text{Cl} \times 10^{-15}$	Perchlorate (µg/L) single	Perchlorate (µg/L) column influent
<b>Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume</b>								
1N/5W-28J2	28J-2	07/01/10	0.8 ± 0.1	-18.3 ± 0.1	-0.1 ± 0.0	102 ± 1	285	261 ± 5
1N/5W-29H1	F6	07/20/10	-0.5	-13.5	0.1	1040 (20)	8.8	12 ± 2
1N/5W-29H3	F6A-S	07/22/10	-0.9	-15.5 ± 0.3	0.2 ± 0.1	NA	0.7	1.1 ± 0.4
1N/5W-33B2	N-10S	07/21/10	1.0 ± 0.0	-12.5 ± 1.7	0.0 ± 0.1	504 (12)	33	27 ± 5
<b>Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume</b>								
1N/5W-21N2	PW-2	08/11/10	1.4 ± 0.1	-16.9 ± 0.4	0.0 ± 0.1	118 (4)	22	21 ± 0
1N/5W-21P2	PW-3	08/10/10	1.1 ± 0.2	-18.0 ± 0.2	0.1 ± 0.1	192 (17)	15	15 ± 0
1N/5W-33B1	N-10D	05/19/11	0.5	-14.1 ± 0.5	0.2 ± 0.0	3640 (200)	1.9	1.6 ± 0.2
1N/5W-34B2	Rialto 02	02/25/12	0.2	-20.3 ± 0.2	0.0 ± 0.0	NA	51	51 ± 1
1N/5W-34B2	Rialto 02 (800')	02/25/12	0.3	-20.1 ± 0.1	0.0 ± 0.0	NA	35	35 ± 1
1N/5W-34G4	PW-5D	08/04/10	0.7 ± 0.4	-17.6 ± 0.6	0.0 ± 0.1	82 (9)	1150	NA
1N/5W-34M1	Rialto 03	03/15/11	0.6 ± 0.3	-15.2 ± 0.1	0.0 ± 0.2	687 (14)	11	12 ± 0
1N/5W-34M1	Rialto 03 (670')	03/15/11	0.6	-14.4 ± 0.1	0.0 ± 0.0	502 (23)	11	11 ± 0
1S/5W-02B3	PW-9C	08/05/10	1.3	-16.1 ± 0.3	0.0 ± 0.1	127 (18)	341	NA
1S/5W-02G1	Rialto 06	03/11/11	1.3 ± 0.3	-16.9 ± 0.2	0.1 ± 0.1	86 (4)	226	239 ± 13
1S/5W-02G1	Rialto 06 (480')	03/11/11	1.0	-17.1 ± 0.0	-0.1 ± 0.1	194 (30)	198	206 ± 13
1S/5W-02G1	Rialto 06 (560')	03/11/11	1.1	-15.7 ± 0.2	0.0 ± 0.1	310 (70)	109	115 ± 13
1S/5W-03A1	Rialto 04	10/20/10	1.1 ± 0.1	-17.6 ± 0.2	0.0 ± 0.2	131 (3)	72	73 ± 2
<b>Wells outside the mapped plume</b>								
1N/5W-17K2	WVWD 24	06/29/10	1.5 ± 0.4	-8.4 ± 0.3	1.2 ± 0.1	6021 (110)	0.3*	0.3 ± 0.0j
1N/5W-27D1	Rialto 01	05/18/11	-0.2 ± 0.1	-15.9 ± 0.2	0.2 ± 0.0	2660 ± 127	3.7	3.8 ± 0.5
1N/5W-33N1	F-49A	04/23/11	-2.4 ± 0.0	-8.5 ± 1.0	2.8 ± 0.2	28,900 (1600)	0.4*	NA
1S/4W-18G1	Colton 15	07/08/10	-12.3 ± 0.7	-4.6 ± 0.1	8.6 ± 0.1	1590 (40)	3.2	3.3 ± 0.1
1S/5W-02K1	WVWD 11	06/30/10	-0.5 ± 0.4	-15.3 ± 0.6	1.0 ± 0.2	66 (3)	9.7	11 ± 1
1S/5W-05A5	F-10C	04/18/11	-4.3 ± 0.2	-9.8 ± 0.5	3.4 ± 0.1	10,200 (400)	0.9*	NA
1S/5W-13B5	13B1-5 (RHSW 5)	08/12/10	-9.8	-7.1 ± 0.1	6.9 ± 0.0	2210 (160)	4.4	4.2 ± 0.1
1N/5W-32A1	F-13A	05/11/11	-5.5 ± 0.2	-4.8 ± 0.0	4.7 ± 0.2	24,200 (1200)	0.4*	0.4 ± 0.0j
<b>Wells in the Chino (or Arlington) subbasins</b>								
1S/5W-23A1	WVWD 42	07/08/10	-10.3 ± 0.1	-7.0 ± 0.0	7.1 ± 0.1	1785 ± 134	1.4	1.4 ± 0.0
1N/5W-32N1	F-26A	12/12/10	-9.7	-8.3 ± 0.0	6.1 ± 0.0	5450 (130)	2.0	1.5 ± 0.2
1N/5W-32N1	F-26A (800')	12/12/10	-9.9	-8.4 ± 0.1	6.2 ± 0.0	5140 (90)	1.6	1.5 ± 0.1
1S/5W-04N1	F-4A	07/28/10	-11.8 ± 0.3	-7.9 ± 0.2	7.6 ± 0.1	1380 (30)	5.8	5.9 ± 1.7
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	NA	12	NA
1S/5W-07R1	F-35A	07/27/10	-11.1	-9.4 ± 0.1	6.4 ± 0.1	415 (15)	0.6	2.4 ± 0.4
1S/5W-14B1	Chino 02	07/22/10	-11.1	-6.8 ± 0.2	7.4 ± 0.0	780 (40)	2.1	1.2 ± 0.8
1S/6W-23D2	F-17B	06/17/10	-13.5 ± 0.0	-6.6 ± 0.3	8.2 ± 0.1	91 ± 4	22	19 ± 0.7
1S/6W-23D2	F-17B (580')	06/17/10	-13.0 ± 0.2	-8.0 ± 0.2	8.1 ± 0.1	100 (4)	20	18 ± 1

NA - data not available

Means and standard deviations are provided for all individual analyses per well. When individual values are provided samples were analyzed once.

$\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  were analyzed by  $\text{O}_2$ -DI-IRMS(+ $\text{N}_2$ ). See Equation 1.4 for definition of  $\Delta^{17}\text{O}$ .

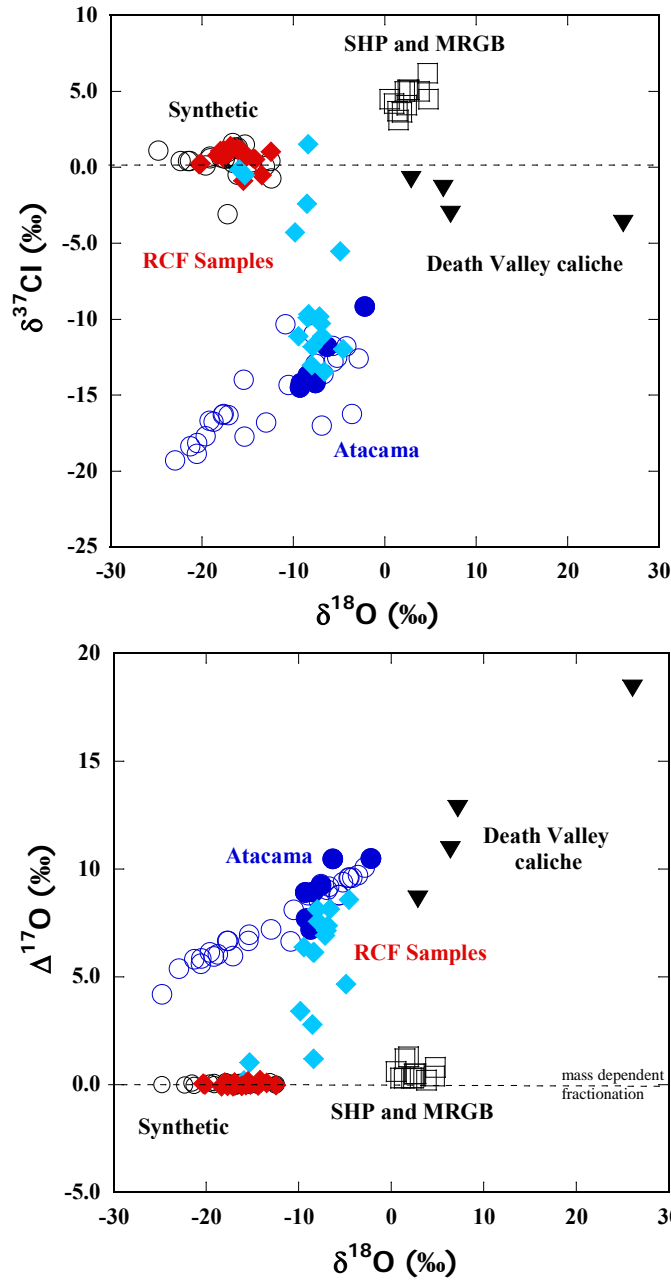
j - estimated value between the MDL and PQL by IC

\* Analysis by IC-MS at Texas Tech University

"Column influent" samples were collected intermittently over a period of hours to days while isotope samples were being loaded onto columns.

"Single" samples were collected once when samples for other chemical and isotopic analyses were collected (Izbicki et al., 2014).

For  $^{36}\text{Cl}$ , values in parentheses are laboratory reported uncertainty for individual samples while +/- values are standard deviations for multiple analyses.



**Figure 3.2.** Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples (red closed diamonds indicate wells located within the mapped  $\text{ClO}_4^-$  plume areas and light blue closed diamonds indicate wells located outside the mapped plume areas; Figure 1.1; Table 3.1; Izbicki et al., 2014) with data for synthetic  $\text{ClO}_4^-$  (open black circles), natural Atacama  $\text{ClO}_4^-$  (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples), and indigenous natural  $\text{ClO}_4^-$  of the southwestern U.S. including Southern High Plains (SHP) and Middle Rio Grande Basin (MRGB) groundwater (black open squares) and Death Valley caliche (black triangles).  $\text{ClO}_4^-$  isotope data from Bao and Gu., 2004; Böhlke et al., 2005; Sturchio et al., 2006, 2012; Böhlke et al., 2009; Jackson et al., 2010; Hatzinger et al., 2011, 2013; unpublished results from SERDP Project ER-1435 for a subset of Atacama field samples. See Section 1.3 for source details.

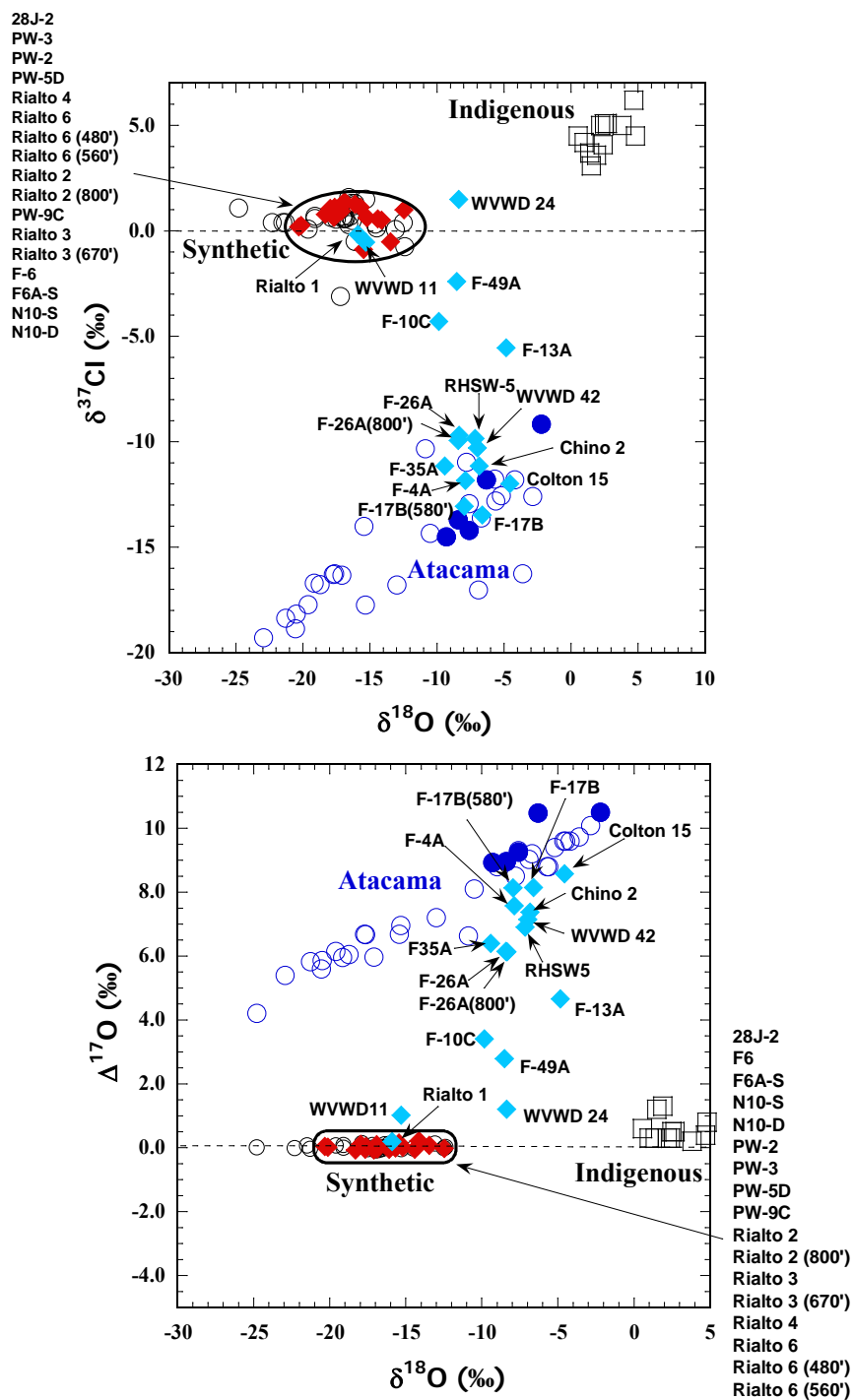
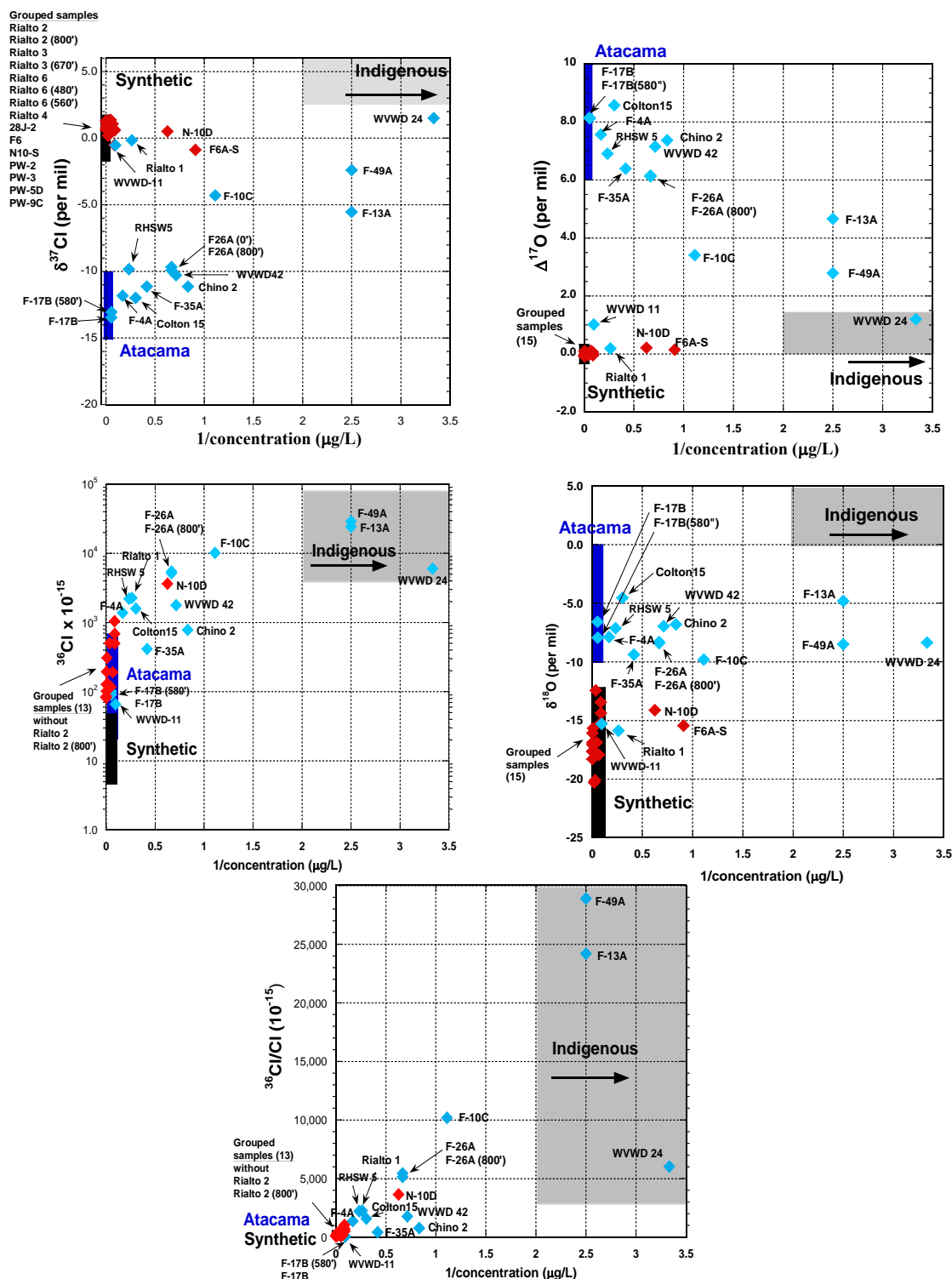


Figure 3.3. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples within the mapped plume areas (red closed diamonds with well designations) and outside the mapped plume areas (light blue closed diamonds) with source data (symbols as described in the caption to Figure 3.2). Sources of  $\text{ClO}_4^-$  isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.





**Figure 3.4.** Comparison of  $\delta^{37}\text{Cl}$  versus  $1/\text{ClO}_4^-$  concentration (top left panel),  $\Delta^{17}\text{O}$  versus  $1/\text{ClO}_4^-$  concentration (top right panel),  $^{36}\text{Cl}/\text{Cl}$  ( $\times 10^{-15}$ ) on log scale versus  $1/\text{ClO}_4^-$  concentration (middle left panel),  $\delta^{18}\text{O}$  versus  $1/\text{ClO}_4^-$  concentration (middle right panel) and  $^{36}\text{Cl}/\text{Cl}$  ( $\times 10^{-15}$ ) on linear scale versus  $1/\text{ClO}_4^-$  concentration (bottom middle panel), with symbols as described in the caption to Figure 3.2. The solid bars (including the wide gray bar for indigenous  $\text{ClO}_4^-$ ) represent typical values for the different sources (see text for explanation). The concentration of indigenous  $\text{ClO}_4^-$  may be lower than indicated on each panel as represented by the arrow. Grouped samples include the list in the upper left unless otherwise noted.

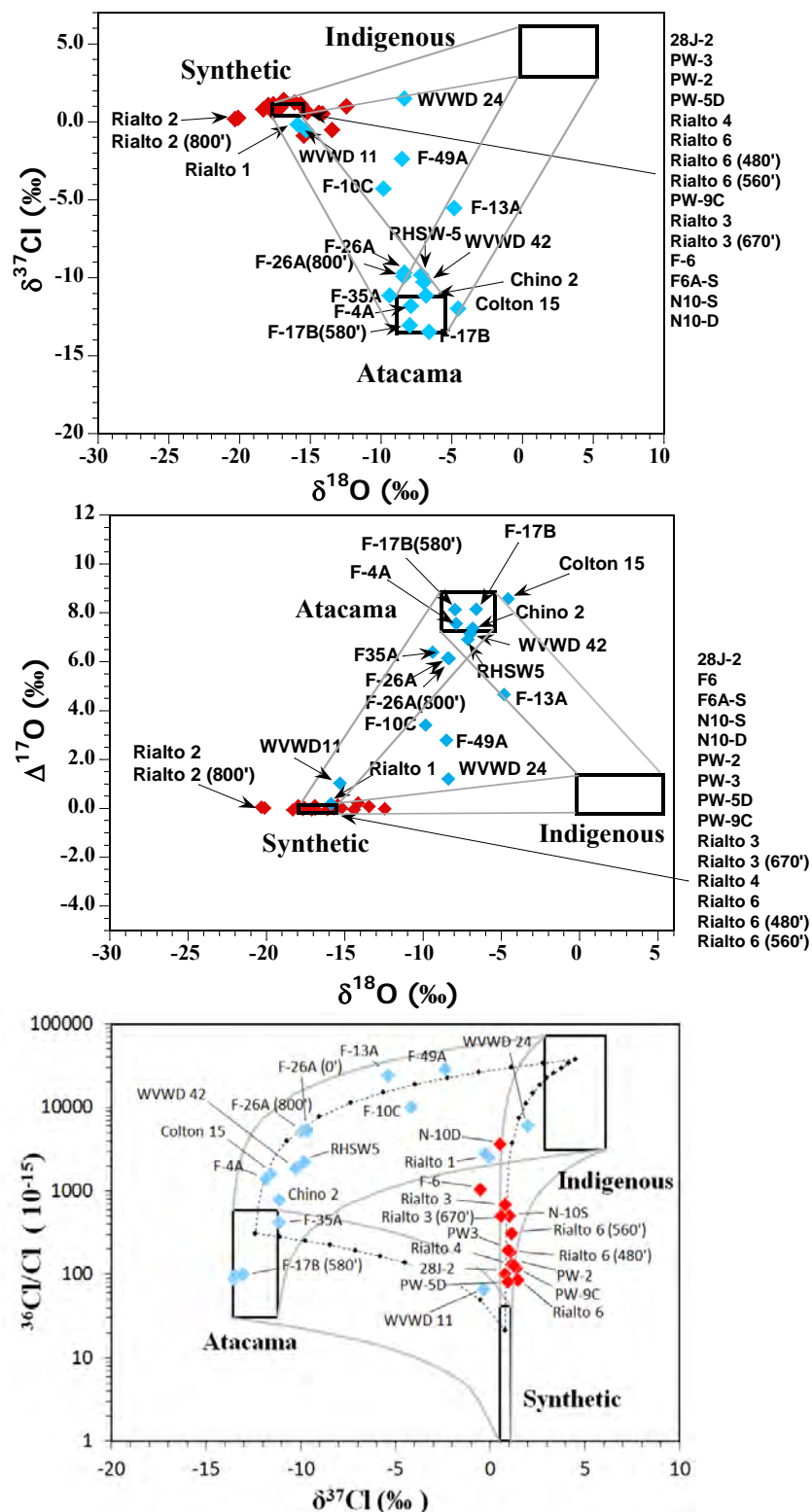


Figure 3.5. Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel);  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (middle panel) and  $\delta^{37}\text{Cl}$  versus  $^{36}\text{Cl}/\text{Cl}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater samples (symbols as in Figure 3.2). The sides of each box represent the endmember value  $\pm 2$ -sigma error and the gray lines represent mixing zones between the endmember regions. The endmember values were determined as detailed in the accompanying text and are provided in Table 3.2. The dotted lines in the bottom panel are hypothetical mixing curves between the three endmembers with tick marks shown every 10% as a function of increasing  $^{36}\text{Cl}/\text{Cl}$  ratio in the mixture (note log scale of y-axis).

**Table 3.2. Isotopic compositions of hypothetical endmembers used for analysis of dominant sources in Study Area groundwater.** The values in parentheses are 2-sigma errors based on regression analysis of local data ( $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  for Atacama and synthetic endmembers) or based on published data ( $\delta^{37}\text{Cl}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  for the indigenous endmember and  $^{36}\text{Cl}/\text{Cl}$  for all endmembers). See text for explanation and sources of data.

<b>Isotope parameter</b>	<b>Atacama <math>\text{ClO}_4^-</math></b>	<b>Synthetic <math>\text{ClO}_4^-</math></b>	<b>Indigenous <math>\text{ClO}_4^-</math></b>
$\delta^{37}\text{Cl}$ (‰)	-12.4 (1.2)	0.8 (0.3)	4.5 (1.6)
$\delta^{18}\text{O}$ (‰)	-7.2 (1.7)	-16.7 (1.1)	2.5 (2.8)
$\Delta^{17}\text{O}$ (‰)	8.1 (0.8)	0.1 (0.1)	0.6 (0.8)
$^{36}\text{Cl}/\text{Cl} \times 10^{-15}$	310 (280)	21 (20)	37,200 (34,000)

**Table 3.3. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $\delta^{37}\text{Cl}$  vs  $\delta^{18}\text{O}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1\_04.xls with as described in Phillips and Gregg, (2001). Endmember values are given in Table 3.2.**

State well number	Local well name	Atacama mixing fraction		Synthetic mixing fraction		Indigenous mixing fraction	
		95% confidence limits maximum	95% confidence limits minimum	95% confidence limits maximum	95% confidence limits minimum	95% confidence limits maximum	95% confidence limits minimum
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-29H1	F6	0.3	-0.1	1.1	0.5	0.3	-0.1
1N/5W-29H3	F6A-S	0.3	-0.1	1.0	0.6	0.2	0.0
1N/5W-33B2	N-10S	0.2	0.0	1.1	0.5	0.4	0.0
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	0.1	-0.1	1.1	0.7	0.2	0.0
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-33B1	N-10D	0.2	0.0	1.1	0.5	0.3	-0.1
1N/5W-34B2	Rialto 02	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34B2	Rialto 02 (800')	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.6	0.3	-0.1
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-02B3	PW-9C	0.2	0.0	1.1	0.7	0.3	-0.1
1S/5W-02G1	Rialto 06	0.2	0.0	1.1	0.7	0.2	0.0
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.1	0.7	0.2	0.0
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.1	0.7	0.3	-0.1
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.2	0.0
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	0.3	-0.1	0.8	0.2	0.5	0.3
1N/5W-27D1	Rialto 01	0.3	-0.1	1.0	0.6	0.2	0.0
1N/5W-33N1	F-49A	0.5	0.1	0.7	0.1	0.5	0.1
1S/4W-18G1	Colton 15	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/5W-02K1	WVWD 11	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-05A5	F-10C	0.6	0.2	0.7	0.1	0.4	0.0
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.0	0.2	0.0
1N/5W-32A1	F-13A	0.7	0.5	0.2	0.0	0.4	0.2
Wells in the Chino (or Arlington) subbasins							
1N/5W-32N1	F-26A	0.9	0.7	0.3	0.1	0.1	-0.1
1N/5W-32N1	F-26A (800')	0.9	0.7	0.3	0.1	0.1	-0.1
1S/5W-04N1	F-4A	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-04N1	F-4A (J613; 2007 sample)	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-07R1	F-35A	1.0	0.8	0.3	0.1	0.1	-0.1
1S/5W-14B1	Chino 02	1.0	0.8	0.2	0.0	0.2	0.0
1S/6W-23D2	F-17B	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/6W-23D2	F-17B (580')	1.1	0.9	0.1	-0.1	0.1	-0.1
	WVWD 42	1.0	0.8	0.2	0.0	0.2	0.0

**Table 3.4. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $\Delta^{17}\text{O}$  vs  $\delta^{18}\text{O}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1\_04.xls as described in Phillips and Gregg, (2001).**

Endmember values are given in Table 3.2.

State well number	Local well name	Atacama mixing fraction		Synthetic mixing fraction		Indigenous mixing fraction	
		95% confidence limits maximum      minimum	95% confidence limits maximum      minimum	95% confidence limits maximum      minimum			
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-29H1	F6	0.2	0.0	1.0	0.6	0.5	-0.1
1N/5W-29H3	F6A-S	0.2	0.0	1.1	0.7	0.3	-0.1
1N/5W-33B2	N-10S	0.2	0.0	1.1	0.5	0.5	-0.1
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	0.2	0.0	1.1	0.7	0.3	-0.1
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-33B1	N-10D	0.2	0.0	1.0	0.6	0.4	0.0
1N/5W-34B2	Rialto 02	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34B2	Rialto 02 (800')	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.6	0.4	0.0
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.6	0.4	0.0
1S/5W-02B3	PW-9C	0.2	0.0	1.0	0.8	0.3	-0.1
1S/5W-02G1	Rialto 06	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.0	0.8	0.3	-0.1
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.2	0.0
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	0.4	0.0	0.6	0.4	0.5	0.3
1N/5W-27D1	Rialto 01	0.2	0.0	1.0	0.6	0.3	-0.1
1N/5W-33N1	F-49A	0.5	0.1	0.5	0.3	0.6	0.0
1S/4W-18G1	Colton 15	1.1	0.9	0.1	-0.1	0.2	0.0
1S/5W-02K1	WVWD 11	0.4	0.0	1.0	0.6	0.3	-0.1
1S/5W-05A5	F-10C	0.7	0.1	0.5	0.3	0.4	0.0
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.0	0.2	0.0
1N/5W-32A1	F-13A	0.9	0.3	0.2	0.0	0.4	0.2
Wells in the Chino (or Arlington) subbasins							
1N/5W-32N1	F-26A	0.9	0.7	0.3	0.1	0.2	0.0
1N/5W-32N1	F-26A (800')	0.9	0.7	0.3	0.1	0.2	0.0
1S/5W-04N1	F-4A	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-04N1	F-4A (J613; 2007 sample)	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-07R1	F-35A	1.0	0.8	0.3	0.1	0.1	-0.1
1S/5W-14B1	Chino 02	1.0	0.8	0.1	-0.1	0.2	0.0
1S/6W-23D2	F-17B	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/6W-23D2	F-17B (580')	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/5W-23A1	WVWD 42	1.0	0.8	0.1	-0.1	0.2	0.0

**Table 3.5. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on  $^{36}\text{Cl}/\text{Cl}$  abundance vs  $\delta^{37}\text{Cl}$  stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1\_04.xls as described in Phillips and Gregg, (2001). Endmember values are given in Table 3.2.**

State well number	Local well name	Atacama mixing fraction		Synthetic mixing fraction		Indigenous mixing fraction	
		95% confidence limits		95% confidence limits		95% confidence limits	
		maximum	minimum	maximum	minimum	maximum	minimum
<u>Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume</u>							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.002	0.001
1N/5W-29H1	F6	0.3	0.0	1.0	0.7	0.03	0.02
1N/5W-29H3	F6A-S	NA*	NA	NA	NA	NA	NA
1N/5W-33B2	N-10S	0.2	0.0	1.0	0.8	0.02	0.01
<u>Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume</u>							
1N/5W-21N2	PW-2	0.2	0.0	1.0	0.8	0.004	0.002
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.006	0.003
1N/5W-33B1	N-10D	0.3	0.0	0.9	0.8	0.12	0.07
1N/5W-34B2	Rialto 02	NA	NA	NA	NA	NA	NA
1N/5W-34B2	Rialto 02 (800')	NA	NA	NA	NA	NA	NA
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.002	0.001
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.8	0.02	0.01
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.8	0.02	0.01
1S/5W-02B3	PW-9C	0.2	0.0	1.0	0.8	0.005	0.002
1S/5W-02G1	Rialto 06	0.2	0.0	1.0	0.8	0.003	0.001
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.0	0.8	0.007	0.002
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.0	0.8	0.02	0.00
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.004	0.002
<u>Wells outside the mapped plume</u>							
1N/5W-17K2	WVWD 24	0.2	0.0	0.9	0.8	0.2	0.1
1N/5W-27D1	Rialto 01	0.3	0.0	0.9	0.8	0.09	0.05
1N/5W-33N1	F-49A	0.5	0.4	0.0	-0.2	1.0	0.6
1S/4W-18G1	Colton 15	1.0	0.9	0.06	0.02	0.04	0.03
1S/5W-02K1	WVWD 11	0.3	0.0	1.0	0.7	0.001	0.000
1S/5W-05A5	F-10C	0.6	0.4	0.4	0.2	0.3	0.2
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.1	0.07	0.04
1S/5W-23A1	F13A	0.7	0.6	0.0	-0.1	0.8	0.5
<u>Wells in the Chino (or Arlington) subbasins</u>							
1N/5W-32A1	WVWD 42	0.9	0.8	0.2	0.0	0.05	0.03
1N/5W-32N1	F-26A	0.9	0.7	0.1	0.0	0.2	0.1
1N/5W-32N1	F-26A (800')	0.9	0.8	0.1	0.0	0.2	0.1
1S/5W-04N1	F-4A	1.0	0.9	0.1	0.0	0.04	0.02
1S/5W-04N1	F-4A (J613; 2007 sample)	NA	NA	NA	NA	NA	NA
1S/5W-07R1	F-35A	1.0	0.8	0.2	0.0	0.01	0.00
1S/5W-14B1	Chino 02	1.0	0.8	0.2	0.0	0.02	0.01
1S/6W-23D2	F-17B	1.1	1.0	0.0	-0.1	0.00	-0.01
1S/6W-23D2	F-17B (580')	1.05	0.97	0.03	-0.04	0.00	-0.01
*NA - data not available.							

Some data from wells within the mapped contaminant plume indicate minor components (0 % to ~ 10 %) of natural indigenous  $\text{ClO}_4^-$ , based upon the values of  $^{36}\text{Cl}/\text{Cl}$  in the samples compared to synthetic  $\text{ClO}_4^-$  sources (Table 3.5). Minor indigenous components were difficult to resolve in the stable isotope endmember mixing model results, because these fractions were small compared to the uncertainties associated with the mixing calculations (Tables 3.3 and 3.4). However, hypothetical mixing curves for  $^{36}\text{Cl}/\text{Cl}$  and  $\delta^{37}\text{Cl}$  with endpoints in synthetic, Atacama, and natural indigenous  $\text{ClO}_4^-$  in Figure 3.5 (bottom panel) highlight an apparent trend of increasing indigenous  $\text{ClO}_4^-$  in the data array from PW5D (0 %) to N10-D (~ 10 %).  $\delta^{18}\text{O}$  values slightly higher than the proposed synthetic endmember (with a  $\delta^{18}\text{O}$  value of  $-16.7 \pm 1.1\text{‰}$ ) are also consistent with varying fractions of indigenous natural  $\text{ClO}_4^-$  in some of the same samples. This general relation is apparent for samples within the mapped plume areas for which both  $\delta^{18}\text{O}$  and  $^{36}\text{Cl}/\text{Cl}$  values are available (Figure 3.6).

Within the mapped plume areas, samples with larger apparent fractions of indigenous  $\text{ClO}_4^-$  based on elevated  $\delta^{18}\text{O}$  and  $^{36}\text{Cl}/\text{Cl}$  ratios (Figure 3.6) tended also to have lower total  $\text{ClO}_4^-$  concentrations (Figure 3.7), consistent with varying fractions of a low-concentration background source. According to a regional statistical study (Fram and Belitz, 2011), in the absence of anthropogenic sources or localized flushing of  $\text{ClO}_4^-$  from the vadose zone by irrigation or other artificial recharge processes, concentrations of indigenous natural  $\text{ClO}_4^-$  in groundwater in arid/semiarid areas of the southwestern U.S. are likely to be less than 1  $\mu\text{g}/\text{L}$ . Where accumulated salts are flushed from the vadose zone, natural  $\text{ClO}_4^-$  concentrations can be much higher, sometimes exceeding 4  $\mu\text{g}/\text{L}$  and occasionally reaching > 50  $\mu\text{g}/\text{L}$ , as reported for irrigated agricultural regions of the SHP (Jackson et al., 2005; Rajagopalan et al., 2006; Rao et al., 2007). Some of the variability observed in Figures 3.6 and 3.7 may reflect differing concentrations of natural background  $\text{ClO}_4^-$  in these wells and variability in synthetic and indigenous endmember isotope values; nevertheless, the general relations are consistent with relatively low background concentrations (<0.5  $\mu\text{g}/\text{L}$ ). The sample from N-10D, with total  $\text{ClO}_4^-$  concentration of 1.6  $\mu\text{g}/\text{L}$ , had a larger apparent fraction of indigenous natural  $\text{ClO}_4^-$  (~ 10 %, based on its  $^{36}\text{Cl}/\text{Cl}$  ratio) than most other wells in the mapped plume area, possibly indicating this sample included groundwater from beneath the contaminant plume, which would be consistent with the deeper screened interval from which the sample was collected.

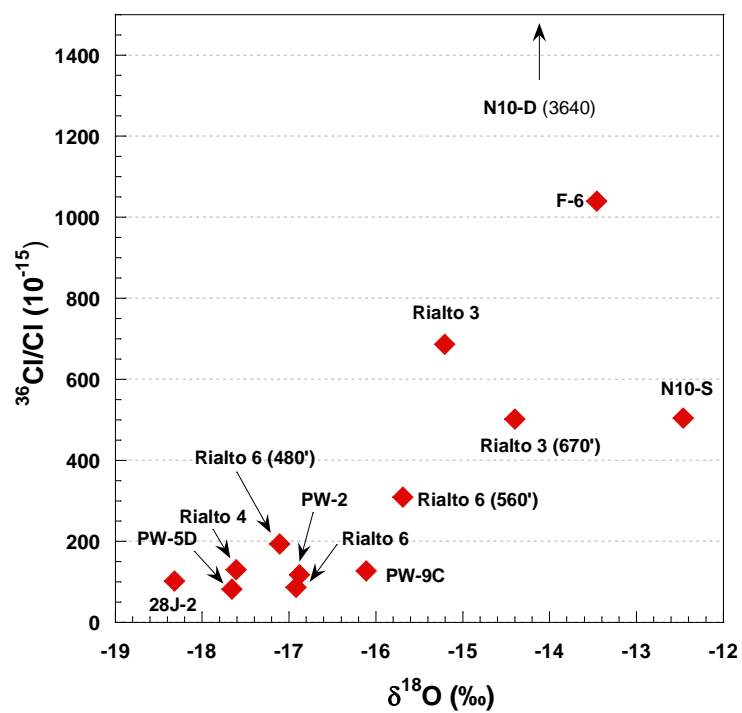


Figure 3.6. Comparison of  $\delta^{18}\text{O}$  values (‰) and  $^{36}\text{Cl}/\text{Cl}$  ratios for wells located within the mapped  $\text{ClO}_4^-$  plumes areas for which both values are available.



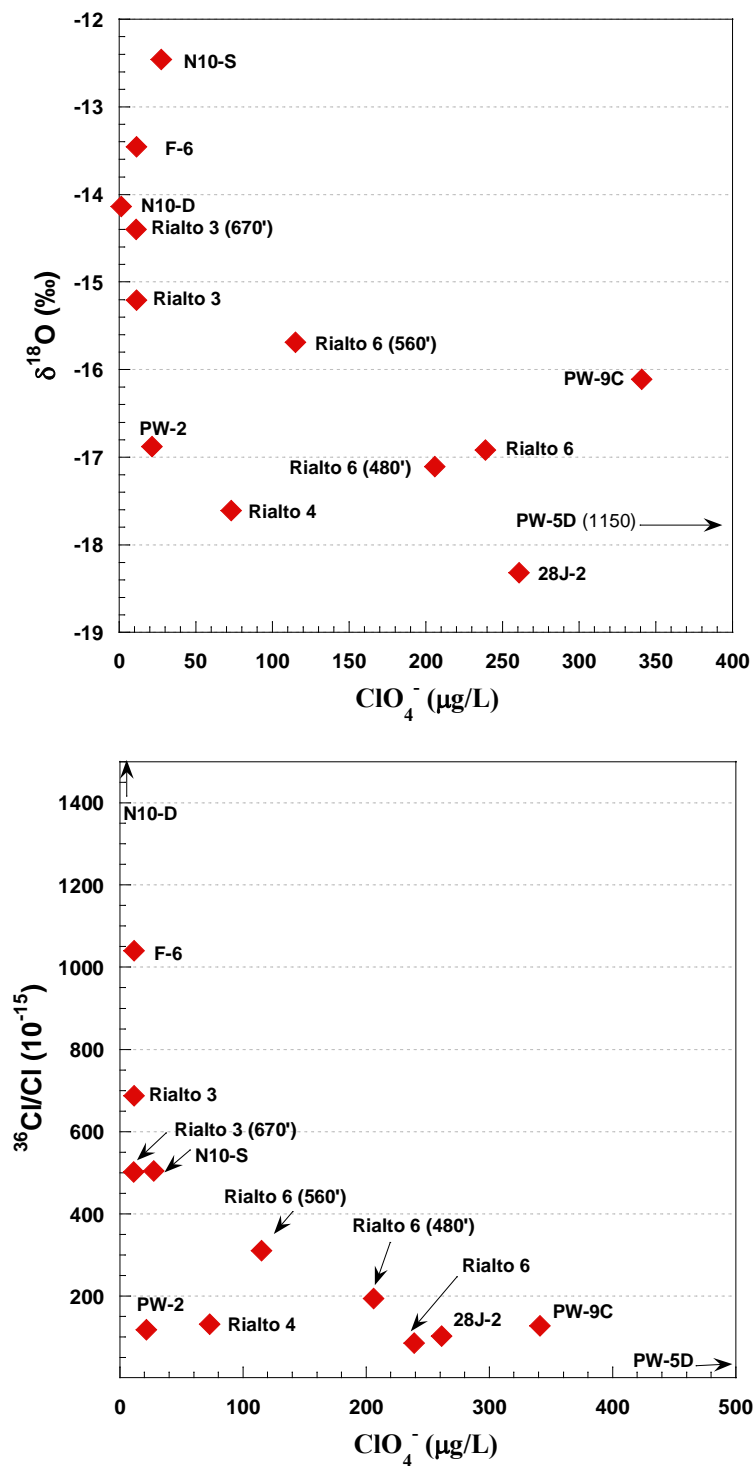


Figure 3.7. Comparison of  $\delta^{18}\text{O}$  value (‰) versus  $\text{ClO}_4^-$  concentration (top panel) and  $^{36}\text{Cl}/\text{Cl}$  ratio vs  $\text{ClO}_4^-$  concentration (bottom panel) for all wells located within the mapped  $\text{ClO}_4^-$  plume areas for which both values are available.

Downgradient from the two mapped plumes in the southeastern direction, parallel to the Rialto-Colton Fault, the dominant source of  $\text{ClO}_4^-$  appears to shift from synthetic to Atacama, presumably because of past fertilizer use in the recharge areas for these groundwaters. The  $\text{ClO}_4^-$  in WVWD 11 appeared to be predominantly synthetic ( $\geq 60\%$  based on mixing fraction analysis), but with a significant fraction of Atacama  $\text{ClO}_4^-$  based upon its  $\Delta^{17}\text{O}$  value of  $\sim +1\text{‰}$ , compared to  $< +0.2\text{‰}$  for all other samples collected in the mapped plume area. WVWD 11 also had a lower  $\delta^{37}\text{Cl}$  value ( $-0.5\text{‰}$ ) than most of the wells that appeared to have predominantly synthetic  $\text{ClO}_4^-$  (average  $+0.6 \pm 0.6\text{‰}$ ). Farther downgradient, wells 13B1-5 (RHSW-5) and Colton 15 appeared to have had  $\text{ClO}_4^-$  that was predominantly Atacama ( $\geq 70\%$ ), based upon their low  $\delta^{37}\text{Cl}$  values ( $-9.8$  and  $-12.3\text{‰}$ , respectively) and elevated  $\Delta^{17}\text{O}$  values ( $+6.9$  and  $+8.6\text{‰}$ , respectively). The combination of low  $\delta^{37}\text{Cl}$  values and high  $\Delta^{17}\text{O}$  values in these samples is characteristic of Atacama-derived  $\text{ClO}_4^-$  (Böhlke et al., 2005, 2009; Jackson et al., 2010; Sturchio et al., 2011, 2012, 2014). The non-Atacama  $\text{ClO}_4^-$  in these samples (RHSW-5, Colton 15) appears to be largely indigenous, based upon elevated  $^{36}\text{Cl}/\text{Cl}$  values and other correlations.

Samples from the Chino subbasin, southwest of the Rialto-Colton Fault, including those from wells WVWD 42, F-17B, F-35A, F-4A, Chino 2, and F-26A, also had isotopic characteristics indicating predominantly Atacama  $\text{ClO}_4^-$  ( $\geq 70\%$  based on mixing fraction calculations), including elevated values of  $\Delta^{17}\text{O}$  ( $+6.1$  to  $+8.2\text{‰}$ ) and low values of  $\delta^{37}\text{Cl}$  ( $-9.7$  to  $-13.5\text{‰}$ ) (Figures 3.3-3.5, Tables 3.3 and 3.4). The finding of  $\text{ClO}_4^-$  derived from Atacama fertilizer in the Chino subbasin is consistent with data from previous studies examining  $\text{ClO}_4^-$  sources in the western region of this subbasin using the stable isotope approach (Sturchio et al., 2008, 2011, 2014). Similarly, Atacama  $\text{ClO}_4^-$  was recently identified in a number of wells in Riverside, CA in the vicinity of the San Bernardino Airport to the southeast of the Study Area using the stable isotope approach Sturchio et al., (2011, 2012). In the latter case, Atacama  $\text{ClO}_4^-$  was identified in wells outside a plume of synthetic  $\text{ClO}_4^-$ . Minor components of indigenous natural  $\text{ClO}_4^-$  also were indicated in some of the Riverside wells based on the stable isotope values.

The detection of Atacama  $\text{ClO}_4^-$  in the Study Area on both sides of the Rialto-Colton Fault and across the Chino subbasin is consistent with the past agricultural history of this area, and with anecdotal evidence of the application of Atacama nitrate fertilizer

throughout this region (Sturchio et al., 2008, 2011, 2012, 2014). A 1949 land use map showing agricultural regions in the Chino Basin, and covering a substantial portion of the Study Area, is provided in Figure 3.8. This map shows the locations of irrigated vineyards, and irrigated and non-irrigated citrus, within the Study Area. Based on the history of this region, it is likely that these areas were in agriculture for at least a few decades before this 1949 map, when application of Atacama fertilizer was common. Additional historical citrus production along Lytle Creek that is not shown on this figure has also been documented (Geologic Associates, 2002). Peak citrus production in the Chino Basin occurred during the period 1930-1950 (USDA, 2013).

Well WVWD 24 was initially selected for sampling as a possible representative of uncontaminated (“background”) conditions, based upon its location far upgradient of the two  $\text{ClO}_4^-$  plume source areas, its low  $\text{ClO}_4^-$  concentration ( $\sim 0.3 \mu\text{g/L}$ ), and its potential for recharge from the San Gabriel Mountains (Izbicki et al., 2014). It was presumed that wells in this part of the Study Area were most likely to contain local indigenous natural  $\text{ClO}_4^-$ , rather than synthetic or Atacama  $\text{ClO}_4^-$ . Three additional wells (F-27A, F-33A, and F-42A) located to the north of WVWD 24 were considered for background sampling, but  $\text{ClO}_4^-$  concentrations in these wells, all of which were monitoring wells, were considered to be too low to obtain adequate  $\text{ClO}_4^-$  for isotopic analysis (0.10, 0.11, and  $0.14 \mu\text{g/L}$ , respectively).

Based on our endmember selections for mixing analysis, isotope data for  $\text{ClO}_4^-$  from WVWD 24 indicated that this well contained a mixture composed primarily of indigenous natural  $\text{ClO}_4^-$  and synthetic  $\text{ClO}_4^-$  (Figures 3.3-3.5, Table 3.3 and 3.4). The sample had a  $\delta^{18}\text{O}$  value of -8.4, which is between the estimated endmember values of synthetic  $\text{ClO}_4^-$  (-16.7 ‰) and indigenous natural  $\text{ClO}_4^-$  (+2.5 ‰) listed in Table 3.2. The WVWD 24 sample had a  $\Delta^{17}\text{O}$  value of +1.5 ‰, which is within the range reported for indigenous natural  $\text{ClO}_4^-$  in the southwest US (Jackson et al., 2010) and slightly lower than that for eastern Oregon (Hatzinger et al., 2012) or the Great Lakes (Poghosyan et al., 2014). Finally, the  $^{36}\text{Cl}/\text{Cl}$  ratio of WVWD 24 ( $6021 \times 10^{-15}$ ) placed it within the lower end of the range reported for indigenous natural  $\text{ClO}_4^-$  (Sturchio et al., 2009; Poghosyan et al., 2014). All of these observations could be consistent with a synthetic-indigenous mixture in WVWD 24. Tritium ( $^3\text{H}$ ) was detected in this well at  $10.6 \text{ pCi/L}$  (Izbicki et al., 2014), indicating that it contained at least some modern (post-bomb) recharge water.

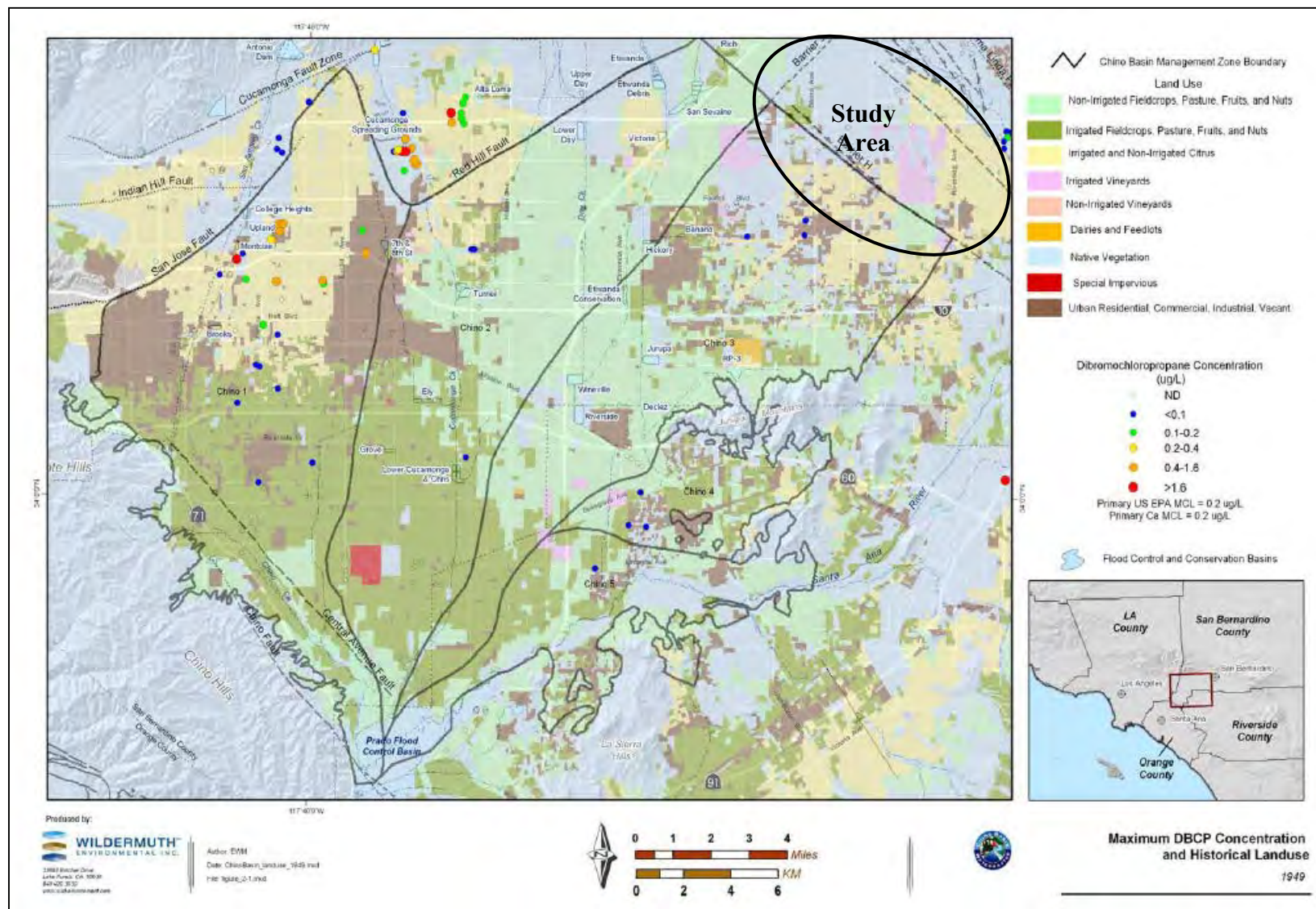
Because WVWD-24 is located upgradient from the identified source areas of the two mapped  $\text{ClO}_4^-$  plumes (Figure 3.1) it is unlikely to have acquired synthetic  $\text{ClO}_4^-$  from those source areas by groundwater flow (Izbicki et al., 2014). If synthetic  $\text{ClO}_4^-$  was present in WVWD 24, as indicated by the isotope data, it may have originated from other commercial sources, such as road flares, fireworks, or blasting explosives, each of which could have contributed to groundwater contamination in this area, as they apparently have elsewhere in the U.S. (e.g., Böhlke et al., 2009; Munster and Hanson, 2009; Munster, 2008; Munster et al., 2008; Aziz et al., 2007).

An alternative hypothesis is that the sample from WVWD 24 represents a local indigenous natural component that is different from the one proposed in the mixing analysis. Additional regional sampling would be required to further evaluate this hypothesis. Moreover, whether  $\text{ClO}_4^-$  from WVWD 24 was entirely or only partly natural (i.e., indigenous mixed with synthetic), it could represent a regional background  $\text{ClO}_4^-$  that is present in varying proportions in other wells in the Study Area that are not within the mapped plumes.

Three wells not discussed above, F-13A, F-49A, and F-10C, all had low  $\text{ClO}_4^-$  concentrations ranging from 0.4 to 0.9  $\mu\text{g/L}$  and appeared to represent mixed  $\text{ClO}_4^-$  sources. In map view (Figure 3.1), well F-13A is located along Barrier H, to the south of the 160 Acre Site, well F-49A is located to the east of Barrier H, and well F-10C is located east of the Rialto-Colton Fault and west of Barrier H. Wells F-10C and F-49A were observed to have perched groundwater cascading downward and mixing with deeper water in the well casing (Izbicki et al., 2014). The perched groundwater may have carried  $\text{ClO}_4^-$  that was not present in deeper groundwater in these wells. Evaluating all three stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^{37}\text{Cl}$ ,  $\Delta^{17}\text{O}$ ), and assuming the characteristics of Atacama, synthetic, and indigenous end members as previously described, the  $\text{ClO}_4^-$  in well F-13A would appear to be composed largely of Atacama and indigenous  $\text{ClO}_4^-$ , whereas wells F10-C and F49-A would appear to have  $\text{ClO}_4^-$  from all three endmember sources, with no individual component dominating the mixture (Tables 3.3 and 3.4). If isotope data from WVWD 24 represented a widespread mixed (indigenous + synthetic) background  $\text{ClO}_4^-$  type, then data from F10-C and F49-A could be consistent with mixtures of Atacama and that mixed background type.

Relations between  $^{36}\text{Cl}/\text{Cl}$  and  $\delta^{37}\text{Cl}$  values (Figure 3.5, bottom panel) generally support the observations above for these wells, but would appear to indicate somewhat larger fractions of indigenous  $\text{ClO}_4^-$  and smaller fractions of synthetic  $\text{ClO}_4^-$ . These apparent differences could be due to variability associated with the  $^{36}\text{Cl}/\text{Cl}$  ratio of natural  $\text{ClO}_4^-$ . Alternatively, it could indicate contributions of anomalously  $^{36}\text{Cl}$ -enriched indigenous  $\text{ClO}_4^-$  from the brief period of thermonuclear bomb tests in the western Pacific (1952-1964). Poghosyan et al. (2014) propose that  $\text{ClO}_4^-$  having  $^{36}\text{Cl}/\text{Cl}$  ratios around  $1,000,000 \times 10^{-15}$  was widely deposited during that time. Most of the samples analyzed in the current study, with the exception of bulk discharge from well F-17B, had measurable  $^3\text{H}$  (Izbicki et al., 2014), indicating at least a portion of the water precipitated after 1952. Any bomb-pulse  $\text{ClO}_4^-$  contribution (if present) would likely be most evident in the lowest-concentration samples (i.e., F-10C, F-13A, F-49A, and WVWD 24); these are the samples having the highest  $^{36}\text{Cl}/\text{Cl}$  ratios in the present study. A potential bomb-pulse contribution is partially accounted for in the indigenous endmember used for mixing calculations (Table 3.2) by inclusion of data from the Great Lakes (Poghosyan et al. 2014). However, it is possible that the  $^{36}\text{Cl}/\text{Cl}$  ratio was actually higher than that assumed for our mixing calculations or that the specific bomb-pulse contribution varied on a well by well basis in relation to varying local recharge conditions.

The origin of the apparent synthetic  $\text{ClO}_4^-$  component in wells F-10C and F-49A (based on stable isotope data) is uncertain, as it contributed a maximum of only about 0.6 and 0.2  $\mu\text{g}/\text{L}$ , respectively, to the mixtures in the wells based on stable isotope mixing fraction estimates (Table 3.3 and Table 3.4). Sources of such low concentrations could include upgradient background groundwater (as in WVWD 24), plume-related or non-plume-related  $\text{ClO}_4^-$  in perched groundwater, or other local contamination. Alternatively, if the  $\text{ClO}_4^-$  in WVWD 24 was isotopically representative of natural indigenous  $\text{ClO}_4^-$  in the Study Area, then the apparent synthetic components in wells F-10C and F-49A would be reduced or eliminated, as these wells fall reasonably in a mixing line between WVWD 24 and the Atacama endmember based on stable isotope values (Figure 3.5). In this case, however, the  $^{36}\text{Cl}/\text{Cl}$  ratios in these two samples would be expected to fall between that of WVWD 24 and the Atacama endpoint, rather than being higher, particularly in the case of well F-49A.

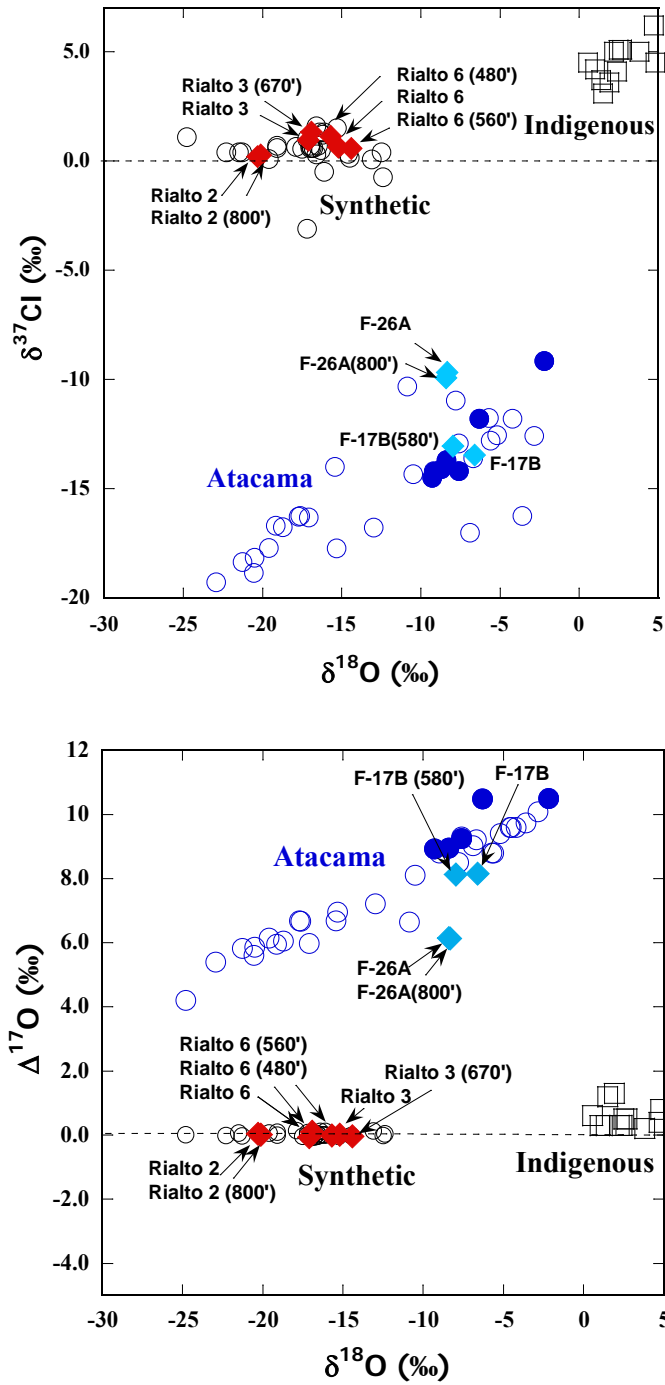


**Figure 3.8. Map of land use characteristics in 1949 in the Chino Basin Management Zone.** The Study Area is shown in the top right corner. Figure from Sturchio et al. (2008).

### 3.3. Depth-Dependent Isotope Samples

Depth-dependent groundwater sampling and isotopic analysis was conducted on five of the production wells in the Study Area: F-17B, F-26A, Rialto 2, Rialto 3, and Rialto 6. This work was conducted as part of the coupled well-bore flow and depth dependent water quality data analysis described by Izbicki et al. (2014). The primary objective of sampling  $\text{ClO}_4^-$  isotopes with depth in these wells was to determine whether different sources were entering the wells at different depth intervals in the aquifer(s) (e.g., synthetic  $\text{ClO}_4^-$  at the top of the well screen and indigenous  $\text{ClO}_4^-$  at a deeper screened interval).

Overall, the results showed that the source(s) of  $\text{ClO}_4^-$  collected from the bulk discharge of each of the wells was similar to that collected from a deep interval within the well, or in the case of Rialto 6, from two different depth intervals (Table 3.1; Figure 3.9). There were small differences in  $\delta^{18}\text{O}$  between F-17B (580') and F-17B (bulk discharge) and between Rialto 6 (480') and Rialto 6 (560'), but these differences did not indicate substantial differences in  $\text{ClO}_4^-$  source fractions. In general, the major-ion composition of the wells with depth also was similar to the surface discharge from each well, with the exception of dissolved oxygen (DO), which generally decreased with depth. Biological degradation of  $\text{ClO}_4^-$  and associated fractionation of Cl and O isotopes in  $\text{ClO}_4^-$  are possible under anoxic conditions, particularly if organic carbon or other electron donors are available for growth of perchlorate-reducing bacteria (e.g., Sturchio et al., 2007). However, depth-dependent discharge data indicate deeper groundwater with low DO may not contribute substantially to the total discharge from the wells (Izbicki et al., 2014). No evidence of  $\text{ClO}_4^-$  isotopic fractionation was apparent in the depth-dependent samples. Similarly, no evidence of  $\text{NO}_3^-$  isotopic fractionation that might be associated with  $\text{NO}_3^-$  reduction was apparent in the same set of samples (Izbicki et al., 2014). For wells F-26A, F-17B, and Rialto 6, both the deep sampled interval and the bulk discharge had high DO concentrations ( $> 8$  mg/L; Izbicki et al., 2014), indicating the bulk of the sampled groundwater was from the upper oxic part of the aquifer. The DO concentration was low for Rialto 3 at 670' (0.2 mg/L) but there was no evidence for biological fractionation of  $\text{ClO}_4^-$  isotopes in this sample. Dissolved oxygen data were not available for Rialto 2 with depth.



**Figure 3.9.** Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from Study Area groundwater depth-dependent samples (symbols as in Figure 3.2) with published data for indigenous natural  $\text{ClO}_4^-$  of the SHP and MRGB (black open squares), natural Atacama  $\text{ClO}_4^-$ , (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples) and synthetic  $\text{ClO}_4^-$  (open black circles). Sources of  $\text{ClO}_4^-$  isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.



### 3.4 Data Quality and Reproducibility

As described in the Methods section, several different procedures were implemented to ensure data quality and reproducibility. These procedures included (1) collection of replicate columns from ~ 30 % of the wells to establish column to column variability; (2) analysis of purified samples multiple times when large enough quantities were available to establish analytical variability; (3) routine analysis of  $\text{ClO}_4^-$  isotopic reference materials for consistency of IRMS data calibration; (4) analysis of  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  by  $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$  in addition to  $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$  to evaluate levels of contaminants and co-products of  $\text{ClO}_4^-$  decomposition; (5) analysis of select samples by  $\text{CO-CF-IRMS}$  for independent quantification of  $\delta^{18}\text{O}$ ; and (6) preparation and analysis of  $\text{ClO}_4^-$  isotopic reference materials loaded onto IX columns to assess effects of routine sample processing on stable isotope values.

#### 3.4.1 Results from Replicate Columns

The data from individual replicate columns are provided in Table 3.6. For  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , differences between replicate columns were  $\leq 0.5$  ‰ for all samples tested. For  $\delta^{37}\text{Cl}$  differences in replicates were  $\leq 1.0$  ‰. For well F-17B, four IX columns were processed and analyzed independently, and the differences among replicates were  $\leq 0.2$  ‰ for  $\delta^{37}\text{Cl}$ ,  $\leq 0.4$  ‰ for  $\delta^{18}\text{O}$  and  $\leq 0.2$  ‰ for  $\Delta^{17}\text{O}$ . Similarly, for the four replicate columns from F-17B,  $^{36}\text{Cl}/\text{Cl}$  ratios varied by  $< 10 \times 10^{-15}$ .

#### 3.4.2 $\delta^{18}\text{O}$ from $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$ , $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$ , and $\text{CO-CFIRMS}$

All samples were analyzed by  $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$  and those results are the reported values (Table 3.1). Most samples also were analyzed by  $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$  to evaluate contaminants and co-products of  $\text{ClO}_4^-$  decomposition such as  $\text{CO}_2$ . A subset of samples also were analyzed independently by  $\text{CO-CF-IRMS}$ , which includes measurement of the relative amount of  $\text{N}_2$  as an indication of potential contamination by air or N-O salts such as  $\text{NO}_3^-$ . For most samples,  $\delta^{18}\text{O}$  values from  $\text{O}_2\text{-DI-IRMS}(+\text{N}_2)$  were slightly lower than  $\delta^{18}\text{O}$  values from  $\text{CO-CF-IRMS}$  and  $\text{O}_2\text{-DI-IRMS}(-\text{N}_2)$  (Figure 3.10; Table 3.7). Several different processes could have contributed to differences between results of these methods including the following: (1) isotopic fractionation of  $\text{O}_2$  by partial oxidation of reduced C in the samples (both  $\text{O}_2\text{-DI-IRMS}$  methods); (2)

isotopically anomalous O<sub>2</sub> produced by fragmentation of CO<sub>2</sub> in the IRMS (O<sub>2</sub>-DI-IRMS(-N<sub>2</sub>)); (3) contamination by O with elevated  $\delta^{18}\text{O}$  (all three methods); (4) isotopic exchange between O<sub>2</sub> and CO<sub>2</sub> in the reaction tubes (both O<sub>2</sub>-DI-IRMS methods); and (5) analytical artifact of elevated CO<sub>2</sub> in the ion source (O<sub>2</sub>-DI-IRMS(-N<sub>2</sub>)). Linear fits through the  $\delta^{18}\text{O}$  data have R<sup>2</sup> values of 0.993-0.994 and intercepts between 0.4 and 0.6 ‰ indicating data from different methods are well correlated. Values of  $\Delta^{17}\text{O}$  were indistinguishable between the two O<sub>2</sub>-DI-IRMS methods, with R<sup>2</sup> of 0.999 and intercept of 0.0 ‰. To illustrate these effects in context of ClO<sub>4</sub><sup>-</sup> source identification, data from all three methods are plotted together with ClO<sub>4</sub><sup>-</sup> source data in Figure 3.11. In most cases, the symbols for isotopic values from each well by each of the three methods overlap. More importantly, the interpretation of sources for all of the wells is the same irrespective of the analytical technique used to measure  $\delta^{18}\text{O}$  and/or  $\delta^{17}\text{O}$ . Data reported in Table 3.1 (from O<sub>2</sub>-DI-IRMS(+N<sub>2</sub>)) represent approximately 100 analyses of separate sample aliquots. A total of three analyses of this type (one from Rialto 4 and two from WVWD 42) were eliminated as outliers (small aliquots, highly fractionated); larger aliquots of those samples subsequently were purified and analyzed. All other analyses were included in the averages.

#### 3.4.3 Perchlorate Extraction and Purification – Method Tests for QA/QC

Quality Assurance/Quality Control (QA/QC) tests were conducted using the USGS37 and USGS38 KClO<sub>4</sub> reference materials to evaluate the extent of Cl and/or O isotopic fractionation caused by the laboratory extraction and purification methods. The methods and results from these tests are presented in Appendix A. Here, isotope data are given for samples subjected to extraction and purification procedures after normalization to analyses of pure reference materials in order to isolate the effects of sample preparation. In summary, values of  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  of USGS37 that had been loaded on IX columns and purified by typical procedures at UIC were within the stated analytical uncertainties of  $\pm 0.2$ ,  $\pm 0.2$ , and  $\pm 0.1$  ‰, respectively, of the assumed reference values for USGS37. For USGS38, which was intentionally synthesized with unnaturally elevated values of  $\delta^{18}\text{O}$  (+52.5 ‰) and  $\Delta^{17}\text{O}$  (+73.3 ‰) and low value of  $\delta^{37}\text{Cl}$  (-87.2 ‰), deviations of -2.1, -1.9 ‰, and +0.6 ‰, respectively, were observed for  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and

$\delta^{37}\text{Cl}$ . Contraction of the apparent O isotope scale (factor of approximately 0.97) is consistent with the presence of small quantities of oxygen-bearing impurities with more normal  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in the prepared samples. The observed deviations in the USGS38 tests, when spread over the entire range of the calibration between USGS37 and USGS38, would not cause significant changes to  $\delta$  values within the ranges of the samples analyzed in this study.

#### 3.4.4 Secondary Ion Mass Spectrometry (SIMS)

An independent analysis of a subset of the purified Study Area  $\text{ClO}_4^-$  samples was conducted by SIMS at the Caltech Microanalysis Center (John Eiler, unpublished data). An advantage of the SIMS method is that much smaller quantities of  $\text{ClO}_4^-$  are required for a SIMS analysis than for traditional IRMS. However, the method has not been validated for complete stable isotope analysis of Cl and O isotopes in  $\text{ClO}_4^-$ , and is considered experimental. The data from the SIMS analysis are compared to those from IRMS for split samples in Appendix B.

**Table 3.6. Perchlorate Cl and O isotope data for replicate sample columns from wells in the Study Area, June 2012 to February 2012.**

State well number	Local well name	Date	$\delta^{37}\text{Cl}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$^{36}\text{Cl}/\text{Cl} \times 10^{-15}$	Column identification number
<b>Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume</b>							
1N/5W-28J2	28J-2	07/01/10	$0.8 \pm 0.1$	-18.2	-0.1	101 (5)	242
1N/5W-28J2	28J-2	07/01/10	0.8	-18.4	-0.1	103 (6)	248
<b>Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume</b>							
1N/5W-21N2	PW-2	08/11/10	$1.4 \pm 0.2$	$-16.9 \pm 0.3$	$0.0 \pm 0.2$	118 (4)	230
1N/5W-21N2	PW-2	08/11/10	1.4	$-16.8 \pm 0.5$	$-0.1 \pm 0.1$	NA	231
1S/5W-03A1	Rialto 04	10/20/10	$1.1 \pm 0.0$	$-17.7 \pm 0.1$	$0.0 \pm 0.2$	131 (3)	269
1S/5W-03A1	Rialto 04	10/20/10	$1.1 \pm 0.1$	$-17.5 \pm 0.2$	$0.0 \pm 0.3$	NA	277
<b>Wells outside the mapped plume</b>							
1N/5W-17K2	WVWD 24	06/29/10	2.0	-8.7	1.1	6021 (110)	223+224+250+251
1N/5W-17K2	WVWD 24	06/29/10	$1.3 \pm 0.0$	$-8.2 \pm 0.2$	$1.3 \pm 0.2$	NA	259+260+261+262
1N/5W-27D1	Rialto 01	05/18/11	$0.0 \pm 0.0$	$-16.1 \pm 0.0$	$0.2 \pm 0.0$	2570 (50)	324
1N/5W-27D1	Rialto 01	05/18/11	$-0.3 \pm 0.1$	$-15.7 \pm 0.0$	$0.2 \pm 0.1$	2750 (40)	325
1S/4W-18G1	Colton 15	07/08/10	$-12.6 \pm 0.4$	$-4.6 \pm 0.1$	$8.6 \pm 0.1$	NA	245
1S/4W-18G1	Colton 15	07/08/10	-11.6	$-4.5 \pm 0.0$	$8.6 \pm 0.1$	1590 (40)	246
1S/5W-02K1	WVWD 11	06/30/10	$-0.3 \pm 0.1$	$-15.4 \pm 0.0$	$1.0 \pm 0.2$	66 (3)	232
1S/5W-02K1	WVWD 11	06/30/10	$-0.7 \pm 0.4$	$-15.2 \pm 0.7$	$1.1 \pm 0.2$	NA	240
1N/5W-32A1	F-13A	05/11/11	-5.4	-4.9	4.4	NA	320
1N/5W-32A1	F-13A	05/11/11	-5.7	$-4.8 \pm 0.0$	$4.8 \pm 0.1$	24200 (1200)	322
<b>Wells in the Chino (or Arlington) subbasins</b>							
1S/5W-23A1	WVWD 42	07/08/10	-10.3	NA	NA	1690 (110)	225
1S/5W-23A1	WVWD 42	07/08/10	-10.3	NA	NA	1880 (90)	226
1S/5W-23A1	WVWD 42	07/08/10	-10.4	$-7.0 \pm 0.0$	$7.1 \pm 0.1$	NA	225 + 226
1S/6W-23D2	F-17B	06/17/10	-13.4	$-6.5 \pm 0.2$	$8.2 \pm 0.1$	92 (6)	238
1S/6W-23D2	F-17B	06/17/10	-13.5	$-6.5 \pm 0.3$	$8.2 \pm 0.1$	88 (5)	239
1S/6W-23D2	F-17B	06/17/10	-13.5	$-6.6 \pm 0.3$	$8.0 \pm 0.0$	88 (6)	243
1S/6W-23D2	F-17B	06/17/10	$-13.6 \pm 0.2$	$-6.9 \pm 0.3$	$8.2 \pm 0.1$	96 (6)	244
1S/5W-04N1	F-4A	07/28/10	$-11.8 \pm 0.3$	$-7.9 \pm 0.2$	$7.6 \pm 0.1$	1380 (30)	255
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	NA	mpg31

NA - data not available.

Means and standard deviations are provided for replicate runs on individual columns. When individual values are provided, samples were analyzed once.

For WVWD-24, columns 223, 224, 250, 251 were combined into a single sample and 259, 250, 261, 262 were combined into a second sample.

The two samples were then treated independently.

Columns 225 & 226 from WVWD 42 were independently analyzed for  $\delta^{37}\text{Cl}$  and  $^{36}\text{Cl}$  but combined for  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  analysis.

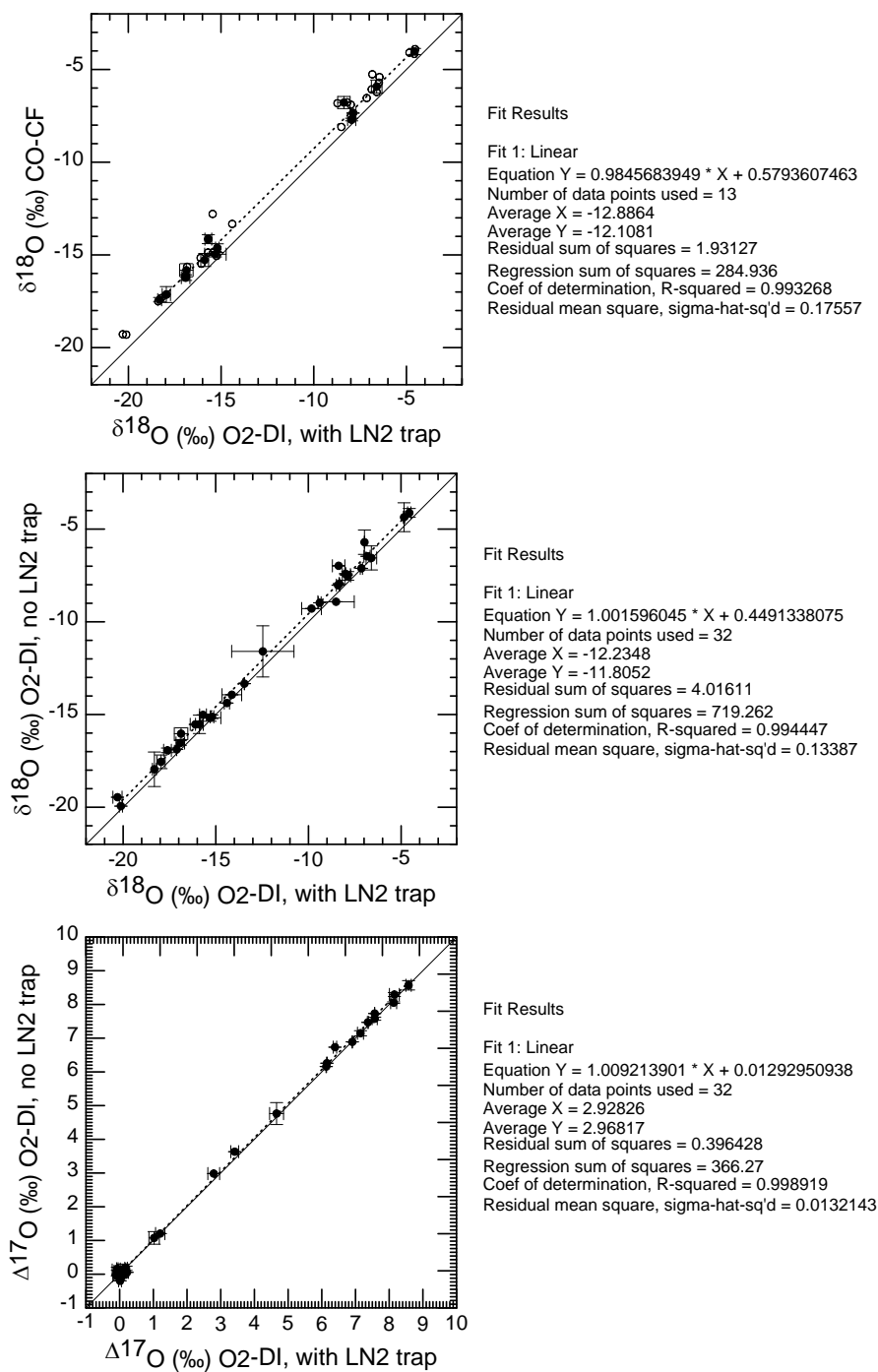
For  $^{36}\text{Cl}$ , values in parentheses are laboratory reported uncertainty for individual samples.

**Table 3.7. Perchlorate isotope data using three different methods of O stable isotope analysis for samples collected from wells in the Study Area, June 2012 to February 2012.**

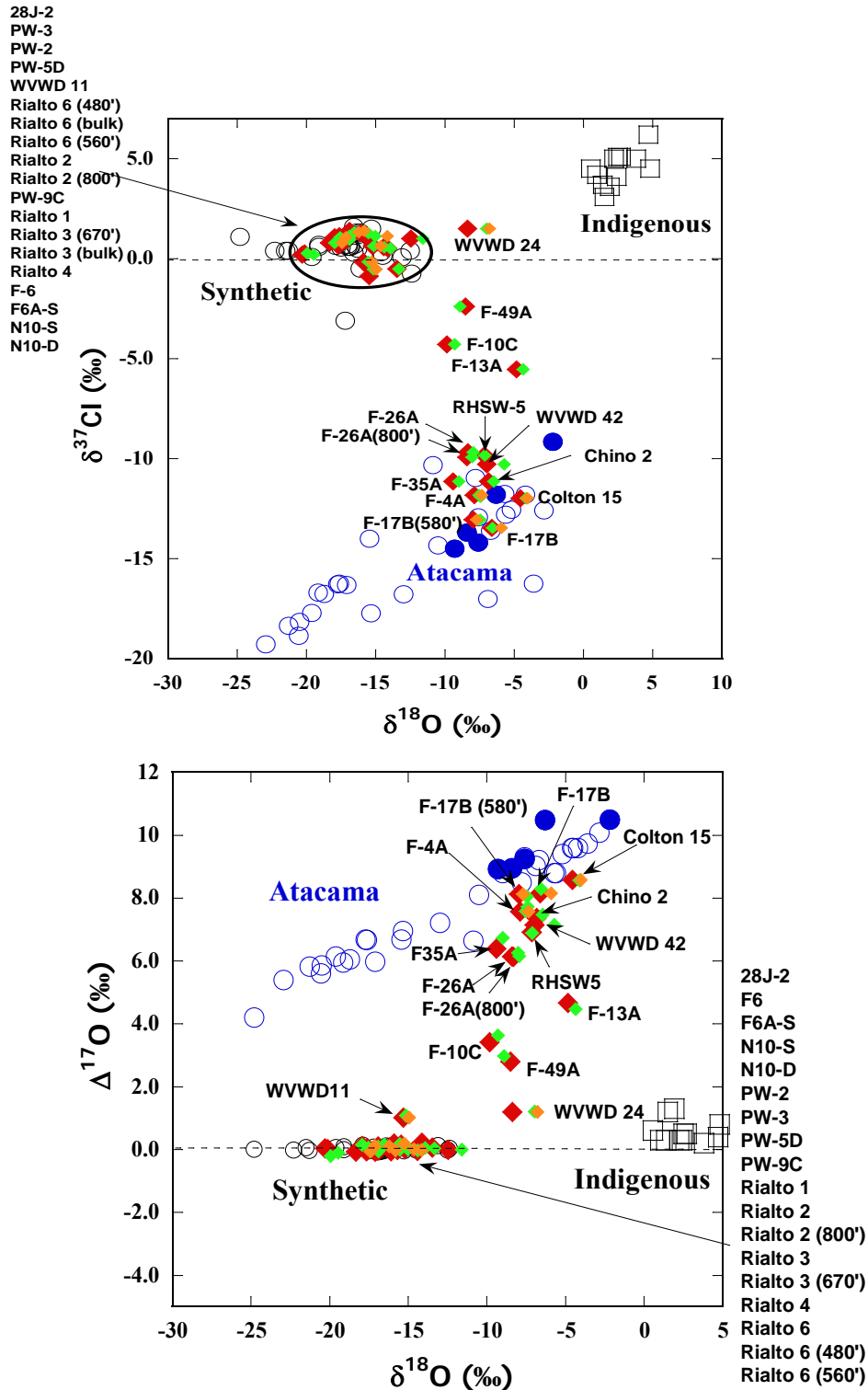
State well number	Local well name	Date	$\delta^{37}\text{Cl}$ (‰)	O <sub>2</sub> -DI-IRMS(+N <sub>2</sub> ) $\delta^{18}\text{O}$ (‰)	O <sub>2</sub> -DI-IRMS(+N <sub>2</sub> ) $\Delta^{17}\text{O}$ (‰)	O <sub>2</sub> -DI-IRMS(-N <sub>2</sub> ) $\delta^{18}\text{O}$ (‰)	O <sub>2</sub> -DI-IRMS(-N <sub>2</sub> ) $\Delta^{17}\text{O}$ (‰)	CO-CFIRMS $\delta^{18}\text{O}$ (‰)
<b>Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume</b>								
1N/5W-28J2	28J-2	07/01/10	0.8 ± 0.1	-18.3 ± 0.1	-0.1 ± 0.0	-18.0 ± 0.9	0.2 ± 0.0	-17.4 ± 0.1
1N/5W-29H1	F6	07/20/10	-0.5	-13.5	0.1	-13.3	0.0	NA
1N/5W-29H3	F6A-5	07/22/10	-0.9	-15.5 ± 0.3	0.2 ± 0.1	NA	NA	NA
1N/5W-33B2	N-10S	07/21/10	1.0 ± 0.0	-12.5 ± 1.7	0.0 ± 0.1	-11.6 ± 1.4	0.0 ± 0.1	NA
<b>Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume</b>								
1N/5W-21N2	PW-2	08/11/10	1.4 ± 0.1	-16.9 ± 0.4	0.0 ± 0.1	16.0 ± 0.3	0.0 ± 0.2	15.8 ± 0.4
1N/5W-21P2	PW-3	08/10/10	1.1 ± 0.2	-18.0 ± 0.2	0.1 ± 0.1	-17.6 ± 0.4	0.1 ± 0.1	-17.1 ± 0.4
1N/5W-33B1	N-10D	05/19/11	0.5	-14.1 ± 0.5	0.2 ± 0.0	-13.9	0.1	NA
1N/5W-34B2	Rialto 02	02/25/12	0.2	-20.3 ± 0.2	0.0 ± 0.0	-19.5	-0.1	NA
1N/5W-34B2	Rialto 02 (800')	02/25/12	0.3	-20.1 ± 0.1	0.0 ± 0.0	-19.9	-0.2	NA
1N/5W-34G4	PW-5D	08/04/10	0.7 ± 0.4	-17.6 ± 0.6	0.0 ± 0.1	NA	NA	NA
1N/5W-34M1	Rialto 03	03/15/11	0.6 ± 0.3	-15.2 ± 0.1	0.0 ± 0.2	-15.1 ± 0.1	0.1 ± 0.1	-14.6 ± 0.2
1N/5W-34M1	Rialto 03 (670')	03/15/11	0.6	-14.4 ± 0.1	0.0 ± 0.0	-14.4	0.0	NA
1S/5W-02B3	PW-9C	08/05/10	1.3	-16.1 ± 0.3	0.0 ± 0.1	-15.5	0.0	NA
1S/5W-02G1	Rialto 06	03/11/11	1.3 ± 0.3	-16.9 ± 0.2	0.1 ± 0.1	-16.5 ± 0.1	0.2 ± 0.1	-16.2 ± 0.2
1S/5W-02G1	Rialto 06 (480')	03/11/11	1.0	-17.1 ± 0.0	-0.1 ± 0.1	-16.9	0.0	NA
1S/5W-02G1	Rialto 06 (560')	03/11/11	1.1	-15.7 ± 0.2	0.0 ± 0.1	-15.0	0.0	-14.2 ± 0.2
1S/5W-03A1	Rialto 04	10/20/10	1.1 ± 0.1	-17.6 ± 0.2	0.0 ± 0.2	-16.9 ± 0.1	0.1 ± 0.1	NA
<b>Wells outside the mapped plume</b>								
1N/5W-17K2	WVWD 24	06/29/10	1.5 ± 0.4	-8.4 ± 0.3	1.2 ± 0.1	-7.0	1.2	-6.8 ± 0.3
1N/5W-27D1	Rialto 01	05/18/11	-0.2 ± 0.1	-15.9 ± 0.2	0.2 ± 0.0	-15.5 ± 0.5	0.2 ± 0.1	-15.3 ± 0.4
1N/5W-33N1	F-49A	04/23/11	-2.4 ± 0.0	-8.5 ± 1.0	2.8 ± 0.2	-8.9	3.0	NA
1S/4W-18G1	Colton 15	07/08/10	-12.3 ± 0.7	-4.6 ± 0.1	8.6 ± 0.1	-4.1 ± 0.2	8.6 ± 0.1	-4.0 ± 0.2
1S/5W-02K1	WVWD 11	06/30/10	-0.5 ± 0.4	-15.3 ± 0.6	1.0 ± 0.2	-15.2 ± 0.2	1.1 ± 0.2	-15.0 ± 0.1
1S/5W-05A5	F-10C	04/18/11	-4.3 ± 0.2	-9.8 ± 0.5	3.4 ± 0.1	-9.3	3.6	NA
1S/5W-13B5	13B1-5 (RHSW 5)	08/12/10	-9.8	-7.1 ± 0.1	6.9 ± 0.0	-7.1	6.9	NA
1N/5W-32A1	F-13A	05/11/11	-5.5 ± 0.2	-4.8 ± 0.0	4.7 ± 0.2	-4.8 ± 0.3	4.5 ± 0.1	NA
<b>Wells in the Chino (or Arlington) subbasins</b>								
1S/5W-23A1	WVWD 42	07/08/10	-10.3 ± 0.1	-7.0 ± 0.0	7.1 ± 0.1	-5.7 ± 0.7	7.1 ± 0.1	NA
1N/5W-32N1	F-26A	12/12/10	-9.7	-8.3 ± 0.0	6.1 ± 0.0	-7.9	6.2	NA
1N/5W-32N1	F-26A (800')	12/12/10	-9.9	-8.4 ± 0.1	6.2 ± 0.0	-8.0	6.3	NA
1S/5W-04N1	F-4A	07/28/10	-11.8 ± 0.3	-7.9 ± 0.2	7.6 ± 0.1	-7.5 ± 0.2	7.6 ± 0.0	-7.3 ± 0.0
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	-7.4	7.7	NA
1S/5W-07R1	F-35A	07/27/10	-11.1	-9.4 ± 0.1	6.4 ± 0.1	-9.0	6.7	NA
1S/5W-14B1	Chino 02	07/22/10	-11.1	-6.8 ± 0.2	7.4 ± 0.0	-6.5	7.5	NA
1S/6W-23D2	F-17B	06/17/10	-13.5 ± 0.0	-6.6 ± 0.3	8.2 ± 0.1	-6.6 ± 0.6	8.3 ± 0.1	-5.9 ± 0.4
1S/6W-23D2	F-17B (580')	06/17/10	-13.0 ± 0.2	-8.0 ± 0.2	8.1 ± 0.1	-7.5 ± 0.0	8.1 ± 0.0	-7.7 ± 0.1

NA - data not available.

Means and standard deviations are provided for all individual analyses per well . When individual values are provided samples were analyzed once.



**Figure 3.10. Comparison of O isotope results from different methods.** Abbreviations for methods are: “CO-CF” = Conversion of O in  $\text{ClO}_4^-$  sample to CO with isotopic analysis of CO by continuous-flow (CF) isotope-ratio mass spectrometry (IRMS); “O<sub>2</sub>-DI” = Conversion of O in  $\text{ClO}_4^-$  to O<sub>2</sub> with isotopic analysis by dual-inlet (DI) IRMS; “with LN<sub>2</sub> trap” = liquid N<sub>2</sub> trap in place to remove condensable gases (e.g., CO<sub>2</sub>, H<sub>2</sub>O) at the inlet to the mass spectrometer; “no LN<sub>2</sub> trap” = liquid N<sub>2</sub> trap removed, admitting condensable gases into the mass spectrometer. Solid lines indicate 1:1 slope (perfect agreement). Dashed lines are linear fits to the data. Open symbols in the upper panel represent samples prepared with TPA and not pre-baked, potentially containing excess C or N (not included in the fit).



**Figure 3.11.** Comparison of  $\delta^{37}\text{Cl}$  versus  $\delta^{18}\text{O}$  (top panel) and  $\Delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  (bottom panel) in  $\text{ClO}_4^-$  from individual Study Area groundwater samples analyzed for O isotopes by  $\text{O}_2$ -DI-IRMS(+ $\text{N}_2$ ) (closed red diamonds),  $\text{O}_2$ -DI-IRMS(- $\text{N}_2$ ) (closed green diamonds), or  $\text{CO}$ -CFIRMS (closed orange diamonds) with published data for natural indigenous  $\text{ClO}_4^-$  of the US (open black squares), natural Atacama  $\text{ClO}_4^-$ , (open blue circles and closed blue circles for actual fertilizer samples) and synthetic  $\text{ClO}_4^-$  (open black circles). Sources of  $\text{ClO}_4^-$  isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.

### 3.5 Summary and Conclusions

Samples were collected from wells throughout the Study Area to evaluate Cl and O stable isotope ratios and  $^{36}\text{Cl}$  abundances in  $\text{ClO}_4^-$ . The dominant source(s) of  $\text{ClO}_4^-$  in each of these samples was evaluated based on the isotopic data. The data indicate that synthetic, Atacama, and indigenous natural  $\text{ClO}_4^-$  were present in groundwater in the Study Area. In general, data for samples with relatively high  $\text{ClO}_4^-$  concentrations were consistent with either synthetic or Atacama  $\text{ClO}_4^-$  being dominant, whereas data for samples with low concentrations were more likely to indicate mixtures including substantial indigenous natural  $\text{ClO}_4^-$  fractions. The stable isotope data from nearly all samples from wells within two mapped  $\text{ClO}_4^-$  contaminant plume areas, including those located in the perched aquifer (28J-2, F6, F6A-S, N-10S) and those in the regional aquifer (PW-2, PW-3, Rialto 2, Rialto 2 (880'), PW-5D, Rialto 3, Rialto 3 (670'), PW-9C, Rialto 6, Rialto 6 (480'), Rialto 6 (560'), and Rialto 4) were consistent with a dominant synthetic  $\text{ClO}_4^-$  source in groundwater. The  $^{36}\text{Cl}$  and  $\delta^{18}\text{O}$  data indicate that some of these samples also contained smaller fractions of indigenous natural  $\text{ClO}_4^-$ . Downgradient from the mapped plume areas at wells 13B1-5 and Colton 15, and across the Rialto-Colton Fault to the southwest (Chino 2, WVWD 42, F-4A, F-35A, F-17B, F-26A, F-26A (800')), the dominant source of  $\text{ClO}_4^-$  in analyzed samples was Atacama, presumably from historical application of fertilizers imported from the Atacama Desert of Chile. Past agricultural land use in these areas is consistent with the use of such fertilizers.

A sample from an upgradient well (WVWD 24) appeared to contain a mixture of synthetic and indigenous  $\text{ClO}_4^-$  based upon all isotopic measures. This sample indicated that other synthetic sources may be present in the Study Area besides those originating from the two mapped plume source locations. There is also a possibility that the  $\text{ClO}_4^-$  in this sample represented a pure indigenous natural source, with isotopic characteristics (primarily  $\delta^{18}\text{O}$ ) that differ from the assumed values; however, the presence of tritium in this sample indicates a synthetic component cannot be ruled out. Interpretation of dominant sources in most samples did not differ substantially if one assumes that WVWD 24 represents a pure indigenous source, although this assumption is likely to affect the estimated fractions of indigenous  $\text{ClO}_4^-$  in mixing calculations.



Isotopic data for samples from wells outside the mapped plume areas with very low  $\text{ClO}_4^-$  concentrations (F-13A, F-49A, and F-10C) indicated mixed  $\text{ClO}_4^-$  sources.  $\text{ClO}_4^-$  from F-13A apparently was composed largely of Atacama and indigenous  $\text{ClO}_4^-$ , with a relatively large fraction of indigenous  $\text{ClO}_4^-$ . A small fraction of synthetic  $\text{ClO}_4^-$  was also possible based upon the  $\delta^{18}\text{O}$  value. Based on the stable isotope values,  $\text{ClO}_4^-$  from F-10C and F-49A appeared to be composed of mixtures of all three sources. However, relations between  $^{36}\text{Cl}/\text{Cl}$  and  $\delta^{37}\text{Cl}$  values could also indicate mixtures of indigenous and Atacama  $\text{ClO}_4^-$ , with no apparent contribution from synthetic  $\text{ClO}_4^-$ . Uncertainties in the interpretation of  $\text{ClO}_4^-$  sources in these low-concentration samples are related in part to uncertainty and possibly local variability in the isotopic characteristics of indigenous natural  $\text{ClO}_4^-$ .

Depth-dependent sampling was conducted in several production wells to determine if different sources of  $\text{ClO}_4^-$  were present in these wells at different depth intervals (e.g., synthetic  $\text{ClO}_4^-$  in shallow groundwater and indigenous  $\text{ClO}_4^-$  in deep groundwater). The isotopic data generally were similar between the bulk discharge of the well and the depth dependent sample(s), indicating little or no variation in major  $\text{ClO}_4^-$  source(s) with depth in these wells.

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## **APPENDIX A**

### **Perchlorate Extraction and Purification – Method Tests for QA/QC**

A total of 27 separate Quality Assurance/Quality Control (QA/QC) tests were performed to evaluate the extent of Cl and O isotopic fractionation caused by the laboratory extraction and purification methods. These tests were done in addition to the field replication tests described in Section 3.4.1. The QA/QC tests were performed by the same analysts who processed all of the field samples at UIC (Abelardo Beloso, Jr. and Linnea Heraty). The perchlorates used in these QA/QC tests were the USGS37 and USGS38  $\text{KClO}_4$  reference materials. A few of the tests included potential interfering compounds, such as chlorate ( $\text{ClO}_3^-$ ) and organics, to measure their effects on  $\text{ClO}_4^-$  isotope ratios.

Twelve tests involved the entire procedure: loading the Purolite A530E ion exchange resin column (i.e., field column) with two liters of a  $\text{KClO}_4$  solution (10 mg/L  $\text{ClO}_4^-$ ), followed by extraction and purification of the  $\text{ClO}_4^-$  from each column according to the procedures used for the field samples. These tests of the entire procedure used the following initial solutions: (1) four columns prepared by loading pure  $\text{KClO}_4$  solutions made from deionized water plus USGS37 (two columns) or USGS38 (two columns); (2) four columns loaded with  $\text{KClO}_4$  solutions made from USGS37 and USGS38 plus added  $\text{ClO}_3^-$  from reagent  $\text{NaClO}_3$  (two columns made with USGS37 and two columns made with USGS38, both having ~1,000 mg/L  $\text{ClO}_3^-$ ); and (3) four columns loaded with  $\text{KClO}_4$  solutions made from USGS37 and USGS38 plus added humic and fulvic acid from commercially available extracts (two columns made with USGS37 and two columns made with USGS38, each having ~50 mg/L humic + fulvic acid). The outcome of these tests for the six column tests having  $\text{ClO}_4^-$  from USGS37 resulted in little isotopic fractionation (Table A-1). The mean normalized values of  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  were within the stated analytical uncertainties of  $\pm 0.2$ ,  $\pm 0.2$ , and  $\pm 0.1$  per mil, respectively, for the calibration values of USGS37. For the six column tests having  $\text{ClO}_4^-$  from USGS38, which was intentionally synthesized with elevated values of  $\delta^{18}\text{O}$  (+52.5 ‰) and  $\Delta^{17}\text{O}$  (+73.3 ‰), and a low value of  $\delta^{37}\text{Cl}$  (-87.2 ‰), the mean normalized values of  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  had deviations of -1.8, -1.7, and +0.6 per mil, respectively. The estimated analytical uncertainties for USGS-38 are  $\pm 0.5$  and  $\pm 0.3$  for  $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$ . The relatively large deviations for the O isotopes in the USGS38 tests may reflect the presence of small amounts of O-bearing impurities which are isotopically light relative to

O in USGS38. If these impurities were present in the USGS37 method test samples, they did not significantly affect the resulting values of  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ . The deviation of the mean normalized  $\delta^{37}\text{Cl}$  value for the USGS38 method tests, +0.6 per mil, is about two standard deviations higher than the accepted value and could be caused by small amounts of gaseous impurities in the  $\text{CH}_3\text{Cl}$  used for Cl isotope ratio measurements. However, the observed deviations in the O and Cl isotope ratios of the USGS38 tests, when spread over the entire range of the calibration between USGS37 and USGS38, would not cause significant changes to  $\delta$  values within the ranges of the samples analyzed in this study.

Other QA/QC tests were done to examine the effects of specific steps in the purification procedure, after the extraction from the Purolite A530E resin (Table A-2). Compared with the deviations described above for the entire extraction and purification procedure, the post-extraction steps caused deviations that were comparable in direction and not significantly different in magnitude from those caused by the entire procedure. This implies that most of the observed isotopic effects associated with extraction and purification of perchlorate samples collected on Purolite A530E resin occur during the post-extraction purification steps, in which there are opportunities for addition of small amounts of O-bearing impurities (or C-bearing impurities that may become oxidized to  $\text{CO}_2$  during the high-temperature  $\text{KClO}_4$  decomposition step) during a number of adsorption, precipitation, and washing steps.

Table A-1. Evaluation of fractionation of Cl and O isotopes during extraction and purification of perchlorate from ion exchange columns.

Test ID	date (mm/yr)	mg ClO4	$\delta^{37}\text{Cl}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$	D37	D18	D17	description of test
UIC-EX1-37C	8/13	3.4	NA	-17.0	0.0	NA	0.0	0.0	USGS-37 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-37D	8/13	3.8	0.9	-17.7	0.0	0.3	-0.6	0.0	USGS-37 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-38C	8/13	3.3	-86.8	50.6	71.6	0.4	-1.9	-1.7	USGS-38 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-38D	8/13	2.8	-86.4	49.3	70.6	0.8	-3.2	-2.7	USGS-38 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-37C	8/13	2.9	0.8	-16.8	0.0	0.2	0.2	0.0	USGS-37 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-37D	8/13	2.8	0.8	-16.6	-0.1	0.2	0.4	-0.1	USGS-37 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-38C	8/13	3.2	-86.5	51.2	72.0	0.7	-1.3	-1.3	USGS-38 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-38D	8/13	2.9	-86.7	50.8	71.7	0.5	-1.7	-1.6	USGS-38 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-37C	8/13	4.2	0.9	-16.9	0.0	0.3	0.1	0.0	USGS-37 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-37D	8/13	3.8	NA	-17.1	0.1	NA	-0.1	0.1	USGS-37 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-38C	8/13	2.7	-86.7	50.5	71.5	0.5	-2.0	-1.8	USGS-38 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-38D	8/13	4.2	NA	51.6	72.3	NA	-1.0	-1.0	USGS-38 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
				USGS-37	mean	0.2	0.0	0.0	
					stdev	0.1	0.4	0.0	
				USGS-38	mean	0.6	-1.8	-1.7	
					stdev	0.2	0.8	0.6	

D37, D18, and D17 are deviations from reference values.  
NA – data not available.  
Reference values of  $\delta^{18}\text{O}$  ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  for USGS37 are -17.0 ‰, 0.0 ‰, and 0.6‰, respectively.  
Reference values of  $\delta^{18}\text{O}$  ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  for USGS38 are 52.5 ‰, 73.3 ‰, and -87.2 ‰, respectively.  
See Equation 1.4 for definition of  $\Delta^{17}\text{O}$ .

Table A-2. Evaluation of fractionation of Cl and O isotopes during specific steps of perchlorate purification and precipitation.

Test ID	date (mm/yr)	mg ClO <sub>4</sub>	$\delta^{37}\text{Cl}$	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$	D37	D18	D17	description of test
RSIL-4 (125A)	11/11	3.1	0.6	-16.9	0.0	0.0	0.1	0.0	USGS-37 stock solution evaporated into combustion tube
RSIL-4 (125B)	11/11	3.1	0.7	-16.6	-0.1	0.1	0.4	-0.1	USGS-37 stock solution evaporated into combustion tube
RSIL-5 (132A)	11/11	3.1	-86.8	51.9	72.3	0.4	-0.6	-1.0	USGS-38 stock solution evaporated into combustion tube
RSIL-5 (132B)	11/11	3.1	-86.2	51.9	72.4	1.0	-0.6	-0.9	USGS-38 stock solution evaporated into combustion tube
RSIL-4 (81410AA)	11/11	1.7	0.7	-16.5	0.1	0.1	0.5	0.1	USGS-37 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-4 (81410AB)	11/11	1.5	0.6	-16.0	0.0	0.0	1.0	0.0	USGS-37 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-5 (92010AA)	11/11	2.1	-87.2	52.1	72.6	0.0	-0.4	-0.7	USGS-38 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-5 (92010AB)	11/11	2.0	-87.2	51.6	71.8	0.0	-0.9	-1.5	USGS-38 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-4 (1 mg ppt)	12/12	0.8	0.4	-16.4	-0.2	-0.2	0.6	-0.2	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-4 (3 mg ppt)	12/12	2.7	0.6	-16.6	-0.1	0.0	0.4	-0.1	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-5 (1 mg ppt)	12/12	0.8	NA	51.2	70.5	NA	-1.3	-2.8	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-5 (3 mg ppt)	12/12	2.7	-86.4	51.0	71.8	0.8	-1.5	-1.5	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC RSIL-4	7/13	2.5	1.3	-17.4	0.0	0.7	-0.4	0.0	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC-RSIL-4-Aug-2013	8/13	2.5	0.9	-17.3	-0.1	0.3	-0.3	-0.1	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC-RSIL-5-Aug-2013	8/13	2.4	-87.0	51.2	72.3	0.2	-1.3	-1.0	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C

D37, D18, and D17 are deviations from reference values.  
NA – data not available.  
Reference values of  $\delta^{18}\text{O}$  ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  for USGS37 are -17.0 ‰, 0.0 ‰, and 0.6‰, respectively.  
Reference values of  $\delta^{18}\text{O}$  ,  $\Delta^{17}\text{O}$ , and  $\delta^{37}\text{Cl}$  for USGS38 are 52.5 ‰, 73.3 ‰, and -87.2 ‰, respectively.  
See Equation 1.4 for definition of  $\Delta^{17}\text{O}$ .

**APPENDIX B**  
**Comparison of Cl and O Stable Isotope Values in  $\text{ClO}_4^-$  by SIMS and IRMS**

A set of sample splits (aliquots of purified  $\text{KClO}_4$ ) were sent to Professor John Eiler of Caltech for isotope ratio measurements using the Cameca ims-7f GEO secondary ion mass spectrometer (SIMS), also known as ion microprobe, at the Caltech Microanalysis Center. The primary strength of SIMS stable isotope analysis is that very small sample quantities are required ( $\mu\text{g}$  quantities). However, the method has yet to be fully validated for analysis of Cl and O isotopes in  $\text{ClO}_4^-$ , so the data and method should be considered experimental for this application. This instrument uses a  $\sim 1$  nA primary  $\text{Cs}^+$  ion beam to sputter the sample surface, which generates secondary ions that are accelerated through a magnetic field to a set of detectors for isotope ratio measurement. The  $\text{KClO}_4$  samples were provided as fine powders and a small amount of each sample was pressed into an indium sample mount for analysis. A thin layer of gold was deposited on the sample surface to prevent sample charging, then the sample mount was placed in the high-vacuum sample chamber of the ion microprobe for isotopic analysis. Analyses were performed by rastering the primary ion beam over a  $50\ \mu\text{m} \times 50\ \mu\text{m}$  area to average out the effects of rough sample surface topography. The measurements of  $^{37}\text{Cl}/^{35}\text{Cl}$  were performed separately from the measurements of  $^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$  under slightly different sets of analytical conditions (i.e., beam tuning and counting time) to optimize results. The results of the SIMS analyses are compared with IRMS results in Table B-1. In a memo accompanying the report of these results by Professor Eiler, he concludes that the SIMS method remains experimental and it should be considered less reliable than the IRMS method.

As previously noted, one of the strengths of SIMS is that it can produce isotope ratio measurements from tiny amounts of sample, much smaller than the amounts used for IRMS measurements. However, this can also be a weakness if the sample being measured is not isotopically homogeneous. With respect to measurements of  $\text{ClO}_4^-$  isotope ratios, the sample is measured in the form of solid  $\text{KClO}_4$ , which is precipitated from an aqueous solution after purification. Because there are small (approximately per mil level) mass-dependent isotopic fractionations of O and Cl between solid  $\text{KClO}_4$  and aqueous  $\text{ClO}_4^-$ , isotopic zoning will inevitably occur during precipitation of the solid phase. This can cause the last fraction of  $\text{KClO}_4$  precipitate to be significantly depleted in the heavier isotopes  $^{18}\text{O}$  and  $^{37}\text{Cl}$  relative to the cumulative solid  $\text{KClO}_4$ . For example,

if the isotopic fractionation factor is such that the solid  $\text{KClO}_4$  is one per mil enriched in  $^{18}\text{O}$  and  $^{37}\text{Cl}$  relative to the aqueous  $\text{ClO}_4^-$ , then when 99% of the aqueous  $\text{ClO}_4^-$  has been removed from solution, the solid being precipitated at that instant is about 5 ‰ depleted in both  $^{18}\text{O}$  and  $^{37}\text{Cl}$  relative to the cumulative solid  $\text{KClO}_4$ . Also, at the initial stage of precipitation, the solid phase is one per mil enriched in  $^{18}\text{O}$  and  $^{37}\text{Cl}$  relative to the aqueous  $\text{ClO}_4^-$ . In addition, trace contaminants that would have relatively little effect on bulk analysis could be heterogeneously distributed in a sample such that a highly focused ion beam could analyze a highly contaminated small portion of the sample. In contrast, during the IRMS measurements, a sample aliquot is transferred to a glass tube in liquid or bulk powder form and the entire aliquot is converted to  $\text{O}_2$  and  $\text{CH}_3\text{Cl}$  for isotopic analysis, thus minimizing effects of trace contaminants or isotopic fractionation during precipitation of the  $\text{KClO}_4$ .



**Table B-1. Comparison of IRMS and SIMS results for split samples collected from the Study Area.**

Well	Local well name	Analytical method	USGS Sample number <sup>1</sup>	$\delta^{37}\text{Cl}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{17}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
1S/5W-02K1	WVWD 11	IRMS	N17910	-0.4	-15.7	-7.3	1.0
1S/5W-02K1	WVWD 11	SIMS (11/2013)	N17910	-3.4	-20.9	-8.4	2.7
1S/6W-23D2	F-17B	IRMS	N17880	-13.5	-6.6	4.5	8.0
1S/6W-23D2	F-17B	SIMS (7/2013)	N17880	-13.3	-5.3	4.5	7.3
1N/5W-32N1	F-26A	IRMS	N19245	-9.7	-8.3	1.7	6.1
1N/5W-32N1	F-26A	SIMS (7/2013)	NA <sup>2</sup>	-11.9	-9.1	-0.8	4.0
1N/5W-32N1	F-26A	SIMS (11/2013)	N19245	-8.7	-11.3	1.3	7.3
1S/5W-04N1	F4A	IRMS	N17914	-11.6	-8.0	3.4	7.6
1S/5W-04N1	F4A	SIMS (7/2013)	N17914	-13.9	1.6	7.1	6.2
1S/5W-04N1	F-4A (J613; 2007 sample)	IRMS	N19688	-11.9	-8.0	3.3	7.6
1S/5W-04N1	F-4A (J613; 2007 sample)	SIMS (11/2013)	N19688	-10.7/-8.6	-15.1	-1.5	6.5
1N/5W-21N2	PW-2	IRMS	N17906	1.4	-17.2	-9.2	-0.1
1N/5W-21N2	PW-2	SIMS (11/2013)	N17906	-2.2	-15.1	-9.2	-1.2
1S/5W-02G1	Rialto 06	IRMS	N17916	1.3	-16.9	-8.8	0.2
1S/5W-02G1	Rialto 06	SIMS (11/2013)	N17916	-7.6	-12.5	-3.4	3.2
	USGS37	IRMS <sup>3</sup>	standard	0.6	-17.0	-9.0	0.0
	USGS37	SIMS <sup>3</sup>	standard	0.6	-17.0	-9.0	0.0
	USGS38	IRMS <sup>3</sup>	standard	-87.2	52.4	102.4	73.3
	USGS38	SIMS (7/2013) <sup>3</sup>	standard	-91.0	53.3	98.8	69.3
	USGS38	SIMS (11/2013) <sup>3</sup>	standard	-87.9	53.7	102.7	72.8

<sup>1</sup> IRMS data are for specific samples (column + purification aliquot) that were split for SIMS analysis with the exception of F-17B, for which the  $\delta^{37}\text{Cl}$  value is from the same resin column but different purification aliquot (see Table 3.6).

<sup>2</sup> It is unclear from the data report whether the F26A sample analyzed on 7/2013 was N19245.

<sup>3</sup> IRMS measurements were calibrated to both USGS37 and USGS38. Values for the calibration standards are provided.

SIMS measurements were calibrated to USGS37, whereas USGS38 was analyzed as an unknown.

$\Delta^{17}\text{O}$  values for USGS38 measured by SIMS were recalculated using Equation 1.4 for consistency with other data in this report

( $\Delta^{17}\text{O}$  values for other samples do not differ significantly with different definitions of  $\Delta^{17}\text{O}$ ).